

THE PHENOMENON
OF
SUPERCONDUCTIVITY

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Dedicated to

PROFESSOR JOHN CUNNINGHAM MCLENNAN, PH.D., LL.D.,
D.Sc. (MANC.), D.Sc. (LIV.), F.R.S.

to whose initiative the University of Toronto owes its
Cryogenic Laboratory

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It is a pleasure to record our obligations to the late Professor Kamerlingh Onnes and his successors at the Leiden Laboratory, who have always been most generous in their attitude to our Laboratory.

PREFACE

This monograph is the result of a need that was felt for a simple but rather comprehensive statement of the methods of producing and measuring low temperatures and an outline of the main facts of superconductivity. The latter phenomenon presents a puzzle which has by no means been solved and which offers a wide field for the imagination of the physicist.

The authors feel that they have entered into the fruits of the work of many others who have previously carried out experiments in the laboratory at Toronto under Professor McLennan. Among these we might mention G. M. Shrum, W. W. Shaver, R. J. Lang, C. D. Niven, L. Matheson, J. H. McLeod, L. E. Howlett, R. G. Hunter, R. C. Jacobsen, A. C. Burton, and C. E. Smith, many of whom carried out the work while holders of scholarships from the National Research Council of Canada.

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INTRODUCTION

The Phenomenon of Superconductivity

In 1911, Sir James Dewar, in dealing with the liquefaction of gases and low temperature research, wrote as follows: "Though *Ultima Thule* may continue to mock the physicist's efforts, he will long find ample scope for his energies in the investigation of the properties of matter at the temperatures placed at his command by liquid air and liquid and solid hydrogen. Indeed, great as is the sentimental interest attached to the liquefaction of these refractory gases, the importance of the achievement lies rather in the fact that it opens out new fields of research and enormously widens the horizon of physical science."¹ Dewar might have added helium to the low temperature liquids, for, while the above words were being written, Kamerlingh Onnes² was performing at Leiden experiments on the liquefaction and solidification of helium which led to the discovery of the phenomenon of superconductivity. The initial discovery was that the electrical resistance of mercury suddenly becomes zero (*i.e.*, immeasurably small) at the boiling point of liquid helium, 4.2°K (−269°C).

According to the commonly accepted theory of the conduction of electricity by metals, the electrical current consists of the movement of a stream of electrons through the metal. Electrical resistance is considered to be due to collisions between electrons and the molecules of the metal—an effect which will become smaller as the heat motion of the molecules becomes less and less. In the article referred to above, Dewar enumerates various physical properties showing very interesting variations at low temperatures, and among them he records the variation in the specific resistance of some fourteen pure metals and a like number of alloys as the temperature is reduced and approaches the lowest point then available. As a general thing curves drawn showing the relation between resistance and temperature for the pure metals indicate that at the

absolute zero of temperature the resistance would become zero. However, Dewar's experiments showed that with the "temperatures attainable with liquid hydrogen the increase in conductivity (decrease in resistance) became less for each decrease of temperature, until a point was reached where the curves bent sharply around and any further diminution of resistance became very small; that is, the conductivity (and resistance) remained finite."

Onnes's discovery for mercury was consequently quite revolutionary and at once various metals and alloys were tested for this anomalous behaviour. The results obtained from these experiments have raised many difficulties for the theoretical treatment of the conduction of electricity through metals. Various pure metals and alloys become superconducting at these low temperatures but each one at a temperature peculiar to itself; many pure metals and alloys show no indication of this anomaly even at the lowest temperature yet attained. Some alloys have been found to become superconducting although none of the components have this property—a phenomenon somewhat paralleling the peculiarity of the Heussler alloys which are strongly ferromagnetic although none of their components are magnetic.

Of course, electrical conductivity is only one of many physical properties which may show anomalies at the temperature at which superconductivity sets in. Experiments on such characteristics as heat expansion, specific heat, moduli of elasticity, *etc.*, have been carefully carried out as the substance passed through its superconducting temperature in order to determine whether or not there takes place at this temperature fundamental changes in the structure of the metals themselves.

In the pages which follow, it is the intention of the authors to present a concise and comprehensive account of the present state of this interesting, though somewhat anomalous, property of superconductivity.

The earlier chapters will deal with (1) the measurement of temperatures below that of liquid air, in order to provide an answer to such questions as "When do you know you reach a temperature of, say, 2°K ?" or "What do you mean by saying that you have reached a temperature of 2°K ?" ; (2) the mechanical production of

low temperatures; and (3) the general laws of the variation of the electrical resistance of various substances with temperature, particularly in the region of low temperatures.

Following this will be given an account of (1) superconducting metals and alloys; (2) superconductivity as related to direct and alternating currents, particularly as to currents of high frequency; and (3) changes in other physical properties which may take place at the superconducting temperature.

The closing chapter will deal with attempts which are being made to give a satisfactory explanation of the phenomena of metallic conduction in the light of these superconductivity anomalies.

CHAPTER I

LOW TEMPERATURE THERMOMETRY

1. Temperature Scales and Measurement of Temperature

Most properties of matter depend on the temperature. The length of a metal bar, the volume of a gas at constant pressure, the volume of a liquid such as mercury or alcohol, the electrical resistance of a wire, *etc.*, vary with the temperature. The value x of any physical quantity depending on the temperature may be used as a measure of the temperature; x may be the number expressing the length of a metal bar, or the volume of a gas, or the resistance of a wire. The number x may, indeed, be called the temperature, but some function $f(x)$ of x may provide a more convenient scale for practical purposes. The temperatures of melting ice and of water boiling under standard conditions have long been recognized as determinate and reproducible "fixed points", and in the widely used centigrade scale of temperatures it has been agreed that these points shall receive respectively the numbers 0 and 100 on the scale. Whatever physical quantity x be chosen to indicate temperatures, we may introduce a linear function of x which is equal to zero when the value of x is that corresponding to the temperature of melting ice, and equal to 100 when the value of x is that corresponding to boiling water. If the values of x at the two fixed points in question be denoted by x_0 and x_{100} , then the temperature corresponding to any value x of the measured quantity is given by the equation

$$(1) \quad t = 100(x - x_0) / (x_{100} - x_0).$$

All centigrade scales will coincide at the two fixed points (written 0°C and 100°C), but not in general elsewhere. Thus $t = 50^\circ\text{C}$ implies the observation of an increase in x equal to 50 per cent. of the total increase between melting ice and boiling water, but it is not to

be expected that, when x is, say, a volume of mercury, the same fractional increase will be observed as when x is a volume of water (with its familiar anomalous expansion) or the resistance of a wire.

The physical quantity, the measurement of which is to provide the temperature scale, may be of a most varied nature. The choice is determined, apart from considerations of accuracy, essentially by the temperature range over which it is proposed to make measurements. For temperatures above the melting point of platinum, no materials are sufficiently refractory for use as "thermometers", and the only methods for measuring very high temperatures are based on the examination of the radiation emitted by the hot body. For the range from a red heat up to the melting point of platinum, it is possible to find resistant materials for the construction of thermometers, though the difficulties of manipulation rapidly increase with the temperature. Between the temperatures of boiling water and red heat a large number of methods are available; this range covers what may be called moderately high temperatures. The ordinary temperature range is from melting ice to boiling water; temperatures in this range are now capable of easy and exact measurement. Below melting ice the temperatures may be called low; it is the lower part of this range of temperatures in which we are particularly interested here, and as the precision of measurement below the boiling point of air is of fundamental importance in modern physics, the methods of thermometry in this range must receive more detailed consideration.

We shall distinguish a temperature scale as empirical when, as above, it is based on some arbitrarily selected specific property of matter such as the expansion of mercury, the variation of electrical resistance of platinum, and so on. An important empirical temperature scale is given by following the variation of pressure ($x=p$) of a gas at constant volume; the centigrade gas scale is defined by:

$$(2) \quad t = 100(p - p_0) / (p_{100} - p_0).$$

The definition is complete when we have chosen the gas to be used and have decided what value of p_0 shall be selected. The standard (centigrade) gas scale of temperatures is given by taking hydrogen at $p_0 = 1$ m. of mercury. In terms of this scale the temperatures of

many fixed points have been determined with great accuracy, and the data so accumulated suffice for the calibration of any other thermometers which may be desired to give readings on this scale.

2. The Absolute or Thermodynamic Scale

Apart from all empirical temperature scales, thermodynamical arguments of a very general nature indicate the possibility of establishing a temperature scale which is independent of specific material properties; this is the scale called absolute. Many physical considerations become greatly simplified if temperatures can be expressed in this scale, *i.e.*, if we can find what function $f(t)$ of the empirical temperature will give the absolute temperature T . Before indicating briefly how this function can be determined, it may not be unnecessary to point out explicitly that, while any reasonable, widely recognized empirical temperature scale (such as the scale of the gas thermometer above) would be quite adequate for classifying the facts of physics, yet it is only when the absolute scale is introduced that these facts can be submitted to that type of theoretical analysis which really constitutes physics.

It will be assumed that the reader is familiar with those portions of thermodynamics which are devoted to the enunciation of the first and second laws and to the illustration of these principles by means of reversible Carnot cycles. The latter, it may be recalled, involve ideal heat engines, *i.e.*, devices for the mutual conversion of heat and mechanical energy. Such an engine in its simplest mode of operation takes a quantity of heat Q from a large heat reservoir at the empirical temperature t , gives a quantity of heat Q' to a second reservoir at temperature t' , and yields the difference $Q - Q'$ as external mechanical work. The efficiency of the engine is measured by the ratio $(Q - Q')/Q$, and if attention is paid to those details of the process which insure reversibility of the cycle, it is not difficult to show that the efficiency depends only on the temperatures t, t' of the heat reservoirs involved; in particular, the efficiency is independent of the working substance in the engine and of the detailed structure of the latter. If $(Q - Q')/Q$ is a function of t, t' , so also is Q/Q' , and we may write

$$(3) \quad Q/Q' = F(t, t').$$

A simple argument (in which a third heat reservoir at a fixed temperature lower than either t or t' is introduced) shows that $F(t, t')$ may be written $f(t)/f(t')$, where the function f is independent of the working substance in the engine. The quantity

$$(4) \quad T = f(t),$$

apart from an arbitrary factor, defines a scale of temperature which, from its simplicity (as a thermodynamic variable) and its independence of the choice of thermometric substance, is called the *absolute scale*.

The above arguments, upon which the existence of the absolute scale depends, are of such a nature as entirely to preclude direct comparison between such an absolute scale and ordinary scales. We are provided with a definite thermometer (*e.g.*, a mercury thermometer) which indicates the temperatures t on any arbitrary scale. To each value of t corresponds one of T , but the determination of the numerical correspondence demands a knowledge of $f(t)$ in (4). This function is obtained by the following argument. Take as the working substance in the heat engine a fluid the thermal properties of which are known functions of t , any empirical temperature. Carry this substance round a Carnot cycle and evaluate the heat Q and the work $Q - Q'$ in terms of the thermal coefficients of the working substance. The efficiency of the engine may now be written down, firstly in terms of the absolute temperatures of the two heat reservoirs, and secondly in terms of Q and $Q - Q'$ so calculated. A comparison of the two expressions gives the connection between t and T in terms of the properties of the working substance in the t -scale. The final result is that

$$(5) \quad \log (T/T_0) = \int_{t_0}^t \frac{1}{s} \left(\frac{\partial p}{\partial t} \right)_v dt,$$

where $s = (C_p - C_v) / \left(\frac{\partial v}{\partial t} \right)_p$; C_p , C_v being the specific heats of the substance at constant pressure and at constant volume, and $\left(\frac{\partial v}{\partial t} \right)_p$,

$\left(\frac{\partial p}{\partial t}\right)_v$, being derived from the p - v - t equation of state for the substance.

The only substances for which we possess equations of state accurately enough known for use in (5) are gases. At temperatures well above the critical point and at sufficiently low pressures, all gases show an approach to a very simple behaviour; in these circumstances we say that the gases become approximately ideal. The concept of an ideal gas is a convenient fiction. It provides a first approximation to the behaviour of a real gas, and in certain circumstances the approximation may be quite good enough for practical purposes; in any case corrections for "departure from ideality" can often be made without difficulty. An ideal gas has the familiar equation of state

$$(6) \quad pv = k(1 + at),$$

where t is given by a thermometer in which the same gas is used to define the temperature scale, a is the coefficient of increase of pressure at constant volume (or the coefficient of increase of volume at constant pressure), and k is a constant given by $p_0 v_0$ where p_0, v_0 are values of pressure and volume at $t = 0$. The value of a when t is on the centigrade gas scale (2) is about $1/273$, a value derived from the ideal behaviour of all gases.

With the equation of state (6) the evaluation of (5) gives, since $C_p - C_v = p_0 v_0 a$,

$$T = T_0(1 + at)/(1 + at_0).$$

Since T_0 is an arbitrary constant it is convenient to put

$$T_0 = 1/a + t_0,$$

which gives

$$T = 1/a + t.$$

Thus the absolute scale, which is also known as the thermodynamic or Kelvin scale, differs from the centigrade (ideal) gas scale by the constant $1/a$. Temperatures on the absolute scale are denoted by °K. The ideal gas scale and the absolute centigrade scale are identical; temperatures on the latter scale are denoted by °C.

The behaviour of real gases at ordinary temperatures approaches that of the ideal gas as the pressure is lowered. If the coefficient of increase of pressure of a gas at constant volume were measured at various pressures and the results extrapolated to zero pressure, the value of α for the ideal gas might be found. This method for the determination of α is, however, not often used as the extrapolation cannot be made very accurately. Now an ideal gas is one in which no forces are exerted between the molecules; the energy of such a gas is all kinetic energy. A change in volume leaves the kinetic energy, and therefore the temperature, unaltered. When the pressure of a real gas is changed, the molecular interactions which are always present cause a small but measurable temperature change (Joule-Thomson effect).^{3a} When this temperature change is determined as a function of the pressure-change in the gas ("porous plug" experiment) the quantity α may be calculated. With $t_0 = 0^\circ\text{C}$ in the above formulae, the value of T_0 , the absolute temperature of the ice point, is found to be 273.1°K . It may not be without interest to illustrate the extent to which the reciprocal values of the pressure coefficients of some actual gases differ from 273.1. For hydrogen, nitrogen, and carbon dioxide at normal temperature and pressure we have respectively 273.03, 272.1, and 268.4 as reciprocals of the pressure co-efficients. The almost ideal behaviour of hydrogen is well shown by these numbers.

3. The International Temperature Scale

The International Committee on Weights and Measures (1927)³ adopted certain "fixed points" to serve as industrial and laboratory standards. In doing so they remark: "It is to be understood that this proposal does not purport to replace the absolute temperature scale. . . . It is intended merely to represent this scale in a practical manner with sufficient accuracy to serve the everyday needs of the laboratories for the purpose of industrial certifications, and is to be regarded as susceptible of revision and amendment as improved and more accurate methods of measurement are evolved."

The International Temperature Scale is defined as follows:

- (1) The absolute centigrade scale, on which the temperature of

melting ice and the temperature of condensing water vapour (both under the pressure of one standard atmosphere) are numbered 0° and 100° respectively, is recognized as the fundamental scale to which all temperatures should ultimately be referable.

(2) The experimental difficulties in the practical realization of the absolute scale have made it expedient to adopt a practical scale known as the International Temperature Scale. This scale conforms to the absolute scale as closely as present knowledge permits, and is designed to be easily and accurately reproducible, giving uniformity in all numerical statements of temperatures.

(3) The International Temperature Scale is based upon a number of reproducible equilibrium temperatures to which numerical values are assigned, and upon the indications of interpolation instruments calibrated at the fixed temperatures according to a specified procedure.

(4) The fixed points and the numerical values assigned to them *for the pressure equal to one standard atmosphere* are as follows:

- (a) The temperature at which liquid and gaseous oxygen are in equilibrium is -182.97°C (the oxygen point).
- (b) The temperature at which ice and air saturated with water vapour are in equilibrium is 0.000°C (the ice point).
- (c) The temperature at which liquid water and its vapour are in equilibrium is 100.000°C (the steam point).
- (d) The temperature at which liquid sulphur and its vapour are in equilibrium is 444.60°C (the sulphur point).
- (e) The temperature at which solid and liquid silver are in equilibrium is 960.5°C (the silver point).
- (f) The temperature at which solid and liquid gold are in equilibrium is 1063°C (the gold point).

Where it is not possible to maintain the pressure at exactly the standard atmosphere, empirical formulae are given for a , c , and d to make the necessary corrections. The last decimal place in the values assigned to the temperatures is significant only as regards the degree of reproducibility of the fixed points on the International Scale. It is not suggested that the values are known to this degree of accuracy on the absolute scale.

(5) The means available for interpolation lead to a division of the scale into four parts.

- (a) From the ice point to 660°C the temperature t is deduced from the resistance R_t of a standard platinum resistance thermometer by means of the formula

$$R_t = R_0(1 + At + Bt^2).$$

The three constants R_0 , A , and B in this formula are to be determined by calibration at the ice, steam, and sulphur points respectively.

- (b) From -190°C to the ice point the temperature t is deduced from the resistance of a standard platinum resistance thermometer by means of the formula

$$R_t = R_0[1 + At + Bt^2 + C(t - 100)t^3].$$

The four constants involved are determined by calibration at the oxygen, ice, steam, and sulphur points.

- (c) From 660°C to the gold point the temperature t is deduced from the electromotive force e of a standard Pt , Pt - Rh thermocouple, one junction being kept at the constant temperature 0°C while the other is at the temperature t defined by

$$e = a + bt + ct^2.$$

The constants a , b , and c are determined by calibration at the freezing point of antimony, 630.5°C , and at the silver and gold points.

- (d) Above the gold point the temperature is measured by comparing the intensity of radiation (of a given wave length) emitted by a black body at the temperature in question with the intensity of the same radiation from the black body at the gold point.

4. Temperatures Below that of Liquid Air

For temperatures below 80°K we have not yet an established "international" scale. To determine temperatures in this region,

the platinum resistance thermometer is the most important instrument. A number of fixed points are available for calibration, and although the determination of these points has received much less attention than that of the fixed points for the region covered by the international scale, we may regard the values as fairly accurately known. In the Physikalische Technische Reichsanstalt⁴ (1924, 1926), the following fixed points were determined by means of the constant volume helium thermometer, corrections being made to reduce the readings to the absolute scale:

		1924	1926
Oxygen	Boiling point.....	90.20°K	90.21°K
Nitrogen	Boiling ".....	77.39	77.39
Nitrogen	Melting ".....		63.12
Hydrogen	Boiling ".....	20.42	20.43
Hydrogen	Melting ".....		14.04

To these may be added the following temperatures established by others:

Neon	Boiling point.....	27.3°K
Neon	Melting ".....	24.5
Argon	Boiling ".....	87.5
Argon	Melting ".....	84.0
Transformation points of solid oxygen.....		23.5, 42.5
" " " nitrogen.....		35.5

Two quadratic relations between resistance and temperature are used in the calibration of the platinum resistance thermometer for this low temperature range. One of these relations covers the range -183°C to -212°C , and the other the range -252.8°C to -259°C ; intermediate temperatures involve special adjustments between the formulae. It has not been found practicable to use one resistance formula over the whole range. A gold resistance thermometer has been used but offers few advantages over the platinum thermometer. Both gold and platinum are unsuitable at very low temperatures, their resistance-temperature curves being so strongly curved that a large number of fixed points would be required to determine them at all accurately. Lead, apart from its mechanical weakness, has some advantages; constantan is suitable for liquid hydrogen temperatures.

Thermocouples are not sensitive enough at these temperatures to serve as standards but are useful as control instruments.

5. The Helium Vapour Pressure Thermometer

Temperatures below 4°K are produced by a bath of liquid helium, and a measurement of the vapour pressure of the helium provides a simple and precise method of determining its temperature. The relation between this vapour pressure and the absolute temperature has formed the subject of extensive research at Leiden.⁵ By using a helium gas thermometer in which the helium is under an extremely low pressure (demanding special devices for its measurement), it was found possible to measure the temperatures corresponding to various values of the vapour pressure down to about 1.5°K. The measurement of still lower temperatures demands an extrapolation of the vapour pressure-temperature curve, and this involves somewhat delicate considerations. By an experimental study of the vapour pressure-temperature curves for ether, mercury, argon, neon, and hydrogen, the most probable continuation of the helium curve was suggested, and the extrapolation carried down to 0.82°K (1922). The familiar thermodynamic relation connecting vapour pressure and absolute temperature is

$$\log p = A' + B' \log T - C'/T.$$

To exhibit several vapour pressure curves on one diagram, it is convenient to replace p and T by the reduced pressure π and the reduced temperature τ :

$$\pi = p/p_c, \quad \tau = T/T_c,$$

where p_c , T_c are the critical pressure and critical temperature for the substance. The vapour pressure equation then becomes

$$\log \pi = A + B \log \tau - C/\tau.$$

In figure 1 are shown such curves for the gases named; these curves, which all intersect at the same point, $T_c/T=1$, $p/p_c=1$, are extended to the triple point, T_{tr} . It is apparent that as the curves depart from the common point each becomes ultimately a straight line; consequently the behaviour of helium was assumed to approximate to that indicated by the dotted portion of the *He* curve.

It was later found that helium has a transformation point at a vapour pressure of 38.65 mm., and different formulae are used for the vapour pressure curves above and below the transformation

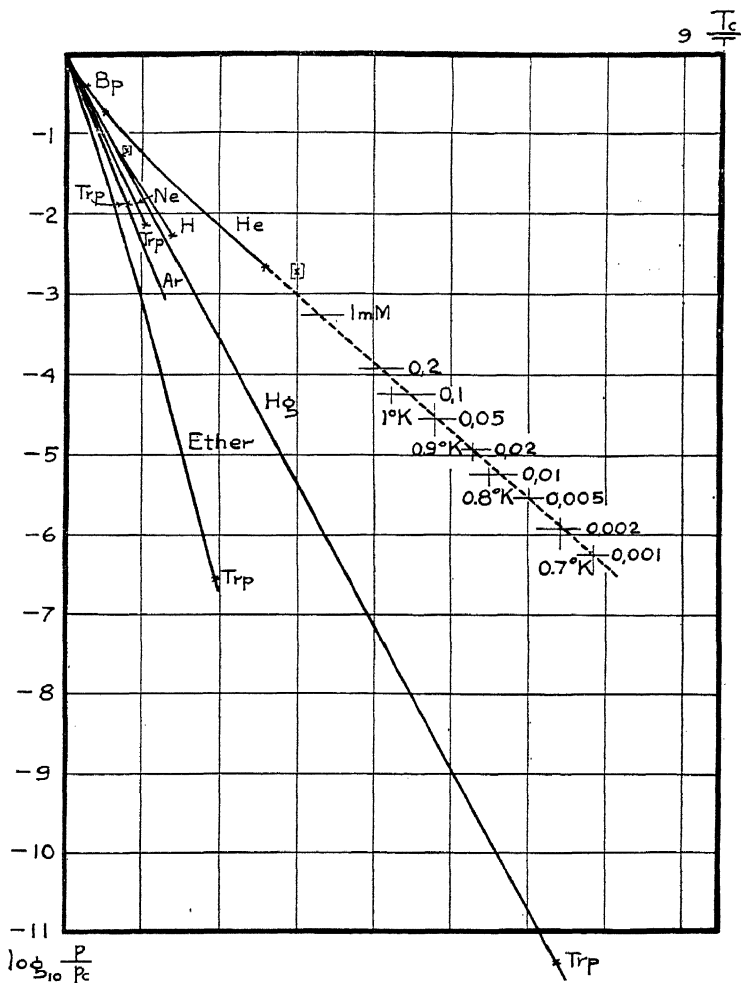


FIG. 1. Showing the Extrapolation of the Helium Vapour Pressure Curve

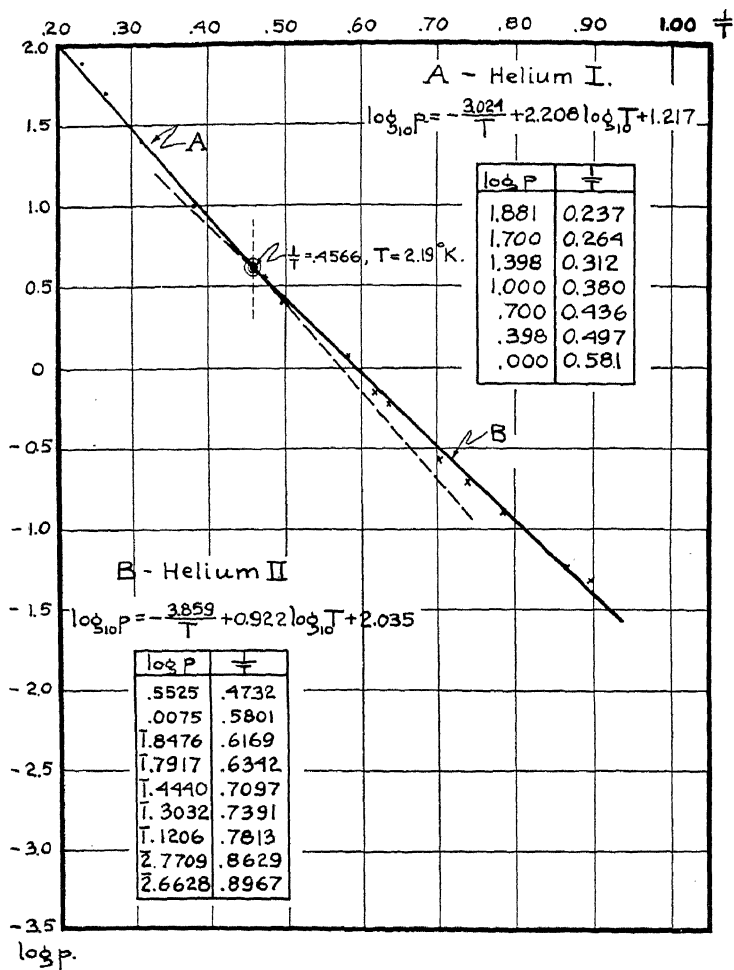


FIG. 2. Showing Vapour Pressure Curves for Helium I and Helium II

temperature, 2.19°K (figure 2). The two intersecting lines in the figure correspond to the expressions:

$$\log p = -3.024/T + 2.208 \log T + 1.217, \text{ for } T \text{ above } 2.19^\circ\text{K},$$

$$\log p = -3.859/T + 0.922 \log T + 2.035, \text{ for } T \text{ below } 2.19^\circ\text{K};$$

p is in cm of mercury and the logarithms are common. These expressions were established in 1929, and formed the basis of temperature measurements in this region until 1932 when slight modifications were thought desirable. The 1929 scale gives the following table which well illustrates the sensitivity of the helium vapour pressure thermometer.⁶

VAPOUR PRESSURE OF LIQUID HELIUM

Vapour pressure cm. of Hg.	Temperature °K	Vapour pressure cm. of Hg.	Temperature °K
132.9	4.899	0.500	1.538
76.00	4.219	0.250	1.393
50.00	3.795	0.1000	1.237
25.00	3.218	0.0500	1.139
10.00	2.636	0.0250	1.055
5.00	2.298	0.0100	0.960
2.50	2.013	0.0050	0.899
1.000	1.714	0.0025	0.844

The corresponding temperatures on the 1932 scale differ from these by less than 0.01° (except at the very lowest pressure) which is about the limit of experimental accuracy in most work.

Just above the liquefaction temperature of helium, the measurement of temperature depends primarily on the gas thermometer and may be measured with an accuracy of .01°, while below this point the measurement may be made with an accuracy of .001° by using the vapour pressure curve for liquid helium.

CHAPTER II

THE PRODUCTION OF LOW TEMPERATURES BY LIQUEFIED GASES

6. Critical Temperatures of Gases

The production of low temperatures is now essentially a problem of liquefying oxygen, nitrogen, hydrogen, and helium on a sufficiently large scale. The experiments of Andrews⁷ showed that for any gas there exists a temperature, its critical temperature, below which it must be cooled before liquefaction becomes possible. The critical temperatures of many gases lie above the ordinary laboratory temperature, and those gases may be liquefied by pressure alone. The farther the temperature of a gas is taken below its critical temperature, the less the pressure necessary to liquefy it.

TABLE OF CRITICAL TEMPERATURES, CRITICAL PRESSURES,* AND BOILING POINTS³

Gases Easily Liquefied				Gases Difficult to Liquefy			
Gas	Critical Temp. °C	Critical Pressure Atmos.	Boiling Point °C	Gas	Critical Temp. °C	Critical Pressure Atmos.	Boiling Point °C
Acetylene	36.0	62.0	- 85	Argon	-122.0	48.0	-185.6
Ammonia	132.4	111.5	- 33.5	Carbon			
Chlorine	144.0	76.1	- 34.6	Monoxide	-139.0	35.0	-190.0
Carbon				Helium	-267.9	2.26	-268.9
Dioxide	31.1	73.0	- 78.2	Hydrogen	-239.9	12.8	-252.7
Ethane	32.1	48.8	- 86.0	Krypton	- 63.0	54.0	-151.8
Ethylene	9.7	50.9	-102.7	Methane	- 82.5	45.8	-164.0
Methyl				Neon	-228.7	25.9	-245.8
Chloride	143.1	65.8	- 24.1	Nitrogen	-147.1	33.5	-195.7
Nitrous				Nitric			
Oxide	36.5	71.7	- 90	Oxide	- 94.0	65.0	-153.0
Sulphur				Oxygen	-118.8	49.7	-182.9
Dioxide	157.2	77.7	- 10.1				
Water	365.0	194.6	100				
Xenon	16.6	58.2	-109.1				

*The Critical Pressure of any gas is the pressure necessary to liquefy the gas at the Critical Temperature.

By compressing chlorine, carbon dioxide, and nitrous oxide and cooling with a freezing mixture, Faraday (1823) liquefied these gases; oxygen, nitrogen, carbon monoxide, and hydrogen, however, resisted the treatment, the critical temperatures of these gases lying considerably below that of any freezing mixture. Success in the liquefaction of gases of the latter class depended on the development of methods of producing very low temperatures.

7. Principles of Methods of Producing Low Temperatures

When a compressed gas is allowed to expand and to perform external mechanical work, the latter is provided at the expense of the heat of the gas (the first principle of thermodynamics), and, if the gas is thermally insulated from its surroundings, it is cooled. The greater the amount of mechanical work done by the gas the greater the cooling. If, for instance, air initially at 20°C does its maximum amount of work in expanding adiabatically from a pressure of 40 atmospheres to a pressure of 1 atmosphere, its temperature, calculated by a simple thermodynamic relation, is reduced to -170°C . The ideal circumstances which enable the maximum work to be done cannot be realized in practice, but the limited cooling available has been successfully employed for the liquefaction of gases.

Although Laplace⁹ had developed the thermodynamic formula for the adiabatic cooling of an expanding gas early in the last century, the result was apparently not regarded as providing a practical means of attaining low temperatures until, in 1877, Cailletet discovered accidentally that he could liquefy several of the so-called permanent gases by suddenly releasing them from a highly compressed state. Mists of liquid oxygen, nitrogen, air, and even hydrogen were momentarily formed when the gases, cooled to -30°C , and under pressures between 200 and 300 atmospheres, were suddenly released. The discontinuous process of Cailletet, permitting only of the observation of a transient liquefaction, may be made continuous in a variety of ways. Both Rayleigh and Onnes suggested that the compressed gas be allowed to do work by driving some kind of engine; and if, in addition, the old idea of the

Siemens temperature exchanger be used, the method may be made continuous. A temperature exchanger is a device for cooling the compressed gas on its way to the engine by means of the expanded and cooled gas leaving the engine. Although the process appears to be very simple, its practical realization represents a real technical achievement on the part of Claude. The Claude liquefier for air is now in very general use, and a brief description of its essential features is given below (see § 10).

At almost exactly the same time as Cailletet's discovery of the intense cooling obtainable by sudden expansion, Pictet¹⁰ announced the successful liquefaction of oxygen by an entirely different method. Liquid sulphur dioxide produced at ordinary temperature by moderate compression was allowed to boil under reduced pressure, the temperature then falling to -65°C . At this temperature carbon dioxide is liquefied by small pressure, and oxygen, strongly compressed, was found by Pictet to be liquefied by the carbon dioxide boiling under reduced pressure. This cascade method of liquefying gases was used by Onnes¹⁰ at Leiden: the gases used in the various steps were methyl chloride, ethylene, and oxygen, and the process made continuous by a suitable arrangement of compressors and temperature exchangers. Liquid oxygen or nitrogen boiling under reduced pressure will not give a temperature below the critical temperatures of hydrogen and helium, and the cascade method has not been extended to give these gases in the liquid form. It has, however, been suggested recently that liquid neon be used to bridge the gap in the process between oxygen and hydrogen (Clusius).¹¹

Quite apart from the cooling of a gas by external work, it is found that when a compressed gas has its pressure reduced by being allowed to escape through a series of fine holes—no external work need be done—its temperature usually falls. The decrease in temperature is small compared with the decrease obtained by the external work method. Occasionally the gas is slightly heated when allowed to expand without doing external work; this is the case with hydrogen and helium at ordinary temperature. But if the initial temperature of the gas is sufficiently low, it is always cooled by "free expansion". This cooling may be called cooling by

internal work to distinguish it from the much greater cooling by external work.

The cooling by internal work produced by a given pressure drop is found to be nearly independent of the pressure, but it rapidly increases when the temperature is lowered. A change of 200 atmospheres in the pressure of air at 0°C lowers the temperature by 45° ; the same change in pressure of air at -90°C lowers the temperature by 100° . Hydrogen and helium, which are, as noted above, slightly warmed by expansion at ordinary temperatures, are cooled when the temperature is initially low enough. The temperature at which a gas is neither heated nor cooled on free expansion is called its inversion temperature. The inversion temperature of hydrogen is about -80°C , and that of helium about -240°C . If the equation of state for a gas is known, the temperature change by internal work—the Joule-Thomson effect—and the inversion temperature can be calculated. It may be noted that an ideal gas is unchanged in temperature by free expansion.

In 1895, Linde in Germany and Hampson in the United States almost simultaneously applied the internal work method to the design of machines for the practical liquefaction of air. The cooling obtained when the gas escapes through a fine valve is amplified, as in the Claude process, by means of temperature exchangers. Brief descriptions of the Linde and the Hampson liquefiers are given below. For the liquefaction of hydrogen and of helium, preliminary cooling of the gases below their inversion temperature is, of course, necessary if this method is to be applied to these gases.

We shall now discuss the practical production of liquid air¹²—the Hampson, Linde, and Claude liquefiers—liquid hydrogen, and liquid helium.

8. Liquid Air—Hampson Liquefier

The simplest device for the liquefaction of air is a machine designed by Hampson and based directly on the Linde method. The diagram (figure 3) shows the construction of the liquefier. Air compressed to about 150 atmospheres enters at *A* and passes down through the Siemen's interchanger *L*, which consists of a coil

of three or four copper tubes in parallel; this vessel offers a means of equalizing the temperature of the incoming warm gas and the escaping cooled gas, hence the name interchanger. The tubes terminate at the valve *V* and the gas is expanded by operating *V* by the

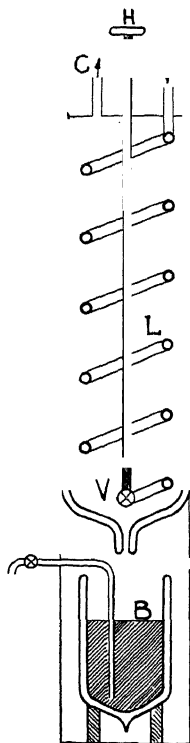


FIG. 3. Hampson Liquefier

handle *H*. The expanded gas returns through *L* and passes back to the compressor at *C*. After a few minutes' operation, the temperature at *V* falls so low that some of the air liquefies. The liquid air is collected at *B* in suitable vacuum containers. This method, an example of so-called regenerative cooling, is simple and serves for the production of about one litre per hour and is often used when a large quantity of liquid air is not desired.

9. Liquid Air—Linde Liquefier

Consideration of efficiency of expansion and compression led Linde to design a high pressure cycle system of liquefaction based on the internal work method of cooling. Figure 4 (a) shows the diagram of the cycle of operations. A low pressure compressor P_1 draws air through a caustic soda purifier D_1 and delivers it at

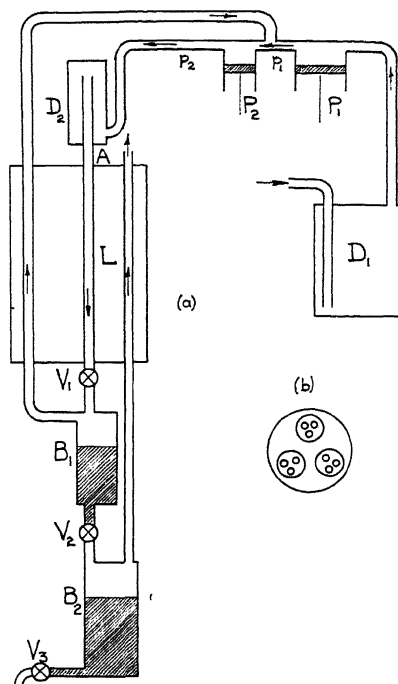


FIG. 4. Linde Liquefier

a pressure p_1 (40 atm.) to a high pressure compressor P_2 that brings the air to the required pressure p_2 (200 atm.).

After passing a calcium chloride desiccator D_2 , the compressed air enters the interchanger L at A , and at the valve V_1 is expanded to the pressure p_1 and returns through L to the intake of the com-

pressor P_2 . A portion is liquefied and collects in B_1 at a temperature about 133°K . It is released intermittently by the valve V_2 to atmospheric pressure when a portion is evaporated to cool the liquid from 133°K to 83°K , the temperature of liquid air at atmospheric pressure. The liquid is collected in B_2 and the evaporated air returns through L to the atmosphere, taking heat from the oncoming high pressure gas. The liquid air is drawn off through V_3 .

In the Linde liquefiers the interchangers are usually constructed of spiral tubes one being drawn through the other and the whole well lagged with mineral wool or other insulating material. A cross section of the pipes in the interchanger is shown at (b) in figure 4.

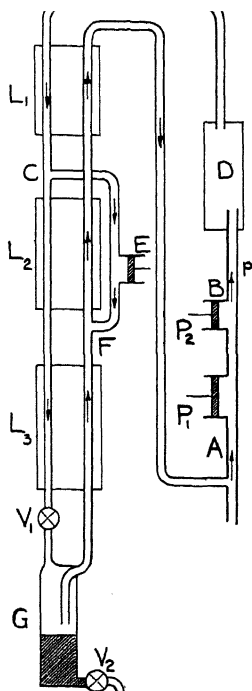


FIG. 5. Claude Liquefier

10. Liquid Air—Claude Liquefier

Claude designed his liquefier with the idea of expanding a portion of the compressed gas in an expansion engine in order to increase the efficiency of the whole system. Figure 5 shows a diagram of the Claude system of liquefying air. Air enters a multiple stage compressor system at A and leaves at B at a pressure p (about 40 atm.) and after passing a caustic soda desiccator D it enters the exchanger L_1 . At C the gas, still at 40 atmospheres pressure, is divided and a part is taken to an expansion engine E where it is expanded doing work on a dynamo or brake system. The other part of the gas continues down through the interchangers L_2 and L_3 to the expansion valve V_1 where it is expanded to atmospheric pressure. A part of the expanded gas is liquefied and collected in the vessel G from which it may be drawn by means of the valve V_2 . The expanded gas leaving G returns through the interchanger L_3 to join the gas coming from the expansion engine at F . This gas then travels up through L_2 and L_1 to the intake of the compressor.

11. Liquid Hydrogen

The critical temperature of hydrogen is 33°K and the critical pressure is 12.8 atmospheres while the inversion point is 193°K. With liquid air boiling at reduced pressure, 63°K may be reached so that using liquid air to cool compressed hydrogen and using expansion with regenerative cooling, hydrogen may be liquefied. This is the usual method. Clusius¹¹ has discussed a cascade system which uses neon as an intermediate refrigerant but suggests that it is only feasible on very large-scale production.

Several liquefiers have been built and described in detail^{13, 14, 15}; we shall describe the one used in the cryogenic laboratory of the University of Toronto which was constructed from the original design of Onnes and differs from it only in minor details. Figure 6 shows the diagram of the liquefier. Pure hydrogen compressed to upwards of 75 atmospheres enters at I and passes successively through the coils L_1 (L_1'), L_2 , L_3 , L_4 , and L_5 . L_1 and L_1' are in parallel and the valve Z regulates the flow through each of them so as to

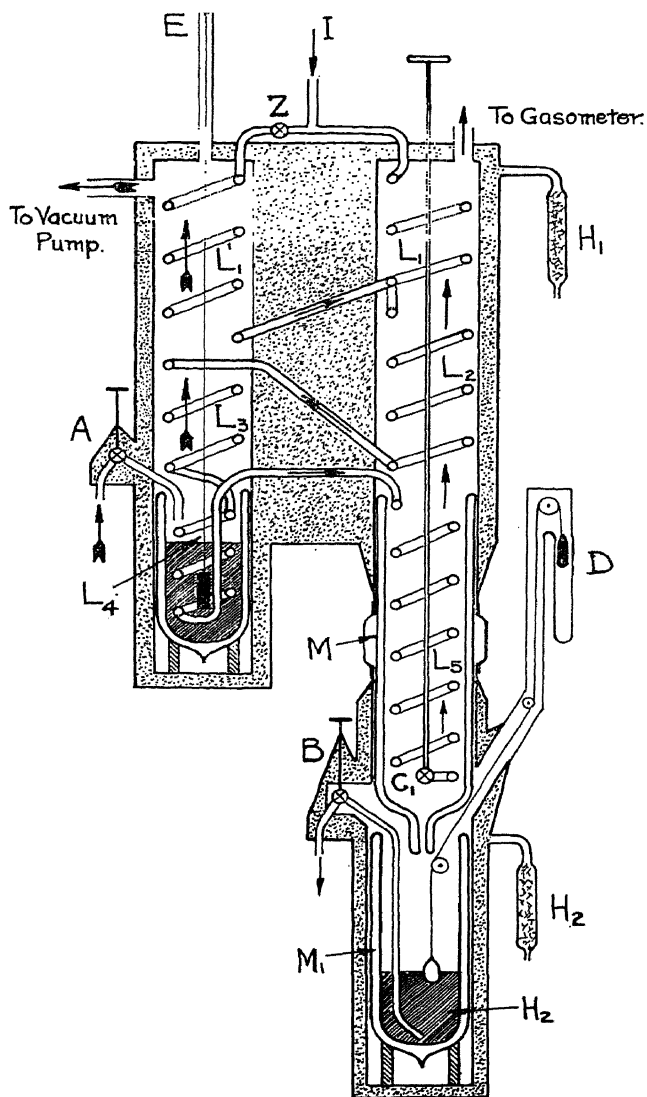


FIG. 6. Hydrogen Liquefier

insure proper interchange of heat between the oncoming compressed gas and the outgoing low pressure gas. The coils L_1 , L_2 , and L_5 are cooled by gaseous hydrogen returning to the gasometers from the expansion valve C_1 . L_1' and L_3 are cooled by evaporated air being drawn off by the vacuum pump and L_4 is partly immersed in liquid air contained in a metal vacuum flask. The valve A serves to draw in more liquid air whenever the float E shows that it is required. Thermocouples attached to the top and bottom of the interchanger L_5 indicate the temperature. The coil L_5 is wrapped in flannel and further protected by the metal flask M . The liquid as it is formed passes through the opening in the bottom of M and is collected in the vacuum flask M_1 . The counterbalanced float D serves to show the level of the liquid in M_1 . Two valves, only one of which, B , is shown, serve to draw off the liquid from M_1 ; they are fitted with long spindles of German silver. The working parts are thus kept at room temperature and work well at all times.

The whole of the liquefier is enclosed in a metal case (either brass or monel metal is suitable) and natural wool is packed tightly all around. Kapok may be used but it is not so good as wool. Drying tubes H_1 and H_2 keep the wool free from moisture condensed in the case. Mercury traps serve to protect the apparatus at all times from an excess of pressure, while rubber safety valves release any sudden or violent increase of pressure.

The liquefier begins to deliver liquid about thirty minutes after being put into operation. The production is 10 to 12 litres of liquid per hour and the consumption of liquid air is about 10 litres per hour. About 10 litres of liquid air serve to cool the liquefier at the start.

12. Liquid Helium—Onnes's Method

By 1908, helium was the only gas which had not been liquefied. Onnes,¹⁶ from his study of the equation of state of helium, concluded that, by precooling with liquid hydrogen boiling at reduced pressure, helium could be liquefied by regenerative expansion. On performing the experiment he was successful in liquefying helium

and so opened the range of temperatures below 15°K for experimental work.

For some years Leiden was the only place where liquid helium and its attendant low temperatures were available. In 1923 McLennan¹⁴ at Toronto liquefied helium in a liquefier modelled after the one at Leiden. In 1925 Meissner¹⁷ at Berlin with a somewhat different arrangement but the same regenerative process liquefied helium. In 1930 at the Bureau of Standards in Washington a liquefier after the Ruhemann¹⁸ plan was put into operation. Since then several other laboratories have liquefied helium and others are building equipment to reach these low temperatures.

The general arrangement of all the continuous cycle helium liquefiers is much the same. The liquefier shown in figure 7 is the one used at Leiden and Toronto and is very similar in design to the hydrogen liquefier. A two-stage compressor compresses helium from a gasometer and the gas passes through desiccators and oil purge to the liquefier.

The compressed gas enters at I and passes successively through the coils $D_1(D_2)$, $D_3(D_4)$, and a charcoal purifier B_1 is attached for removing the last traces of air after the gas passes D_3, D_4 . The gas then enters $D_5(D_6)$, $P_1(P_2)$ in parallel and then passes through P_3 and P_4 and is expanded at the valve M . D_1, D_3, D_5, P_2 , and P_4 serve as interchangers for the expanded helium and D_2, D_4, D_6, P_1 , and P_3 are cooled by the vaporized hydrogen that is drawn off by the vacuum pumps. The coil P_3 is partly immersed in liquid hydrogen boiling at reduced pressure and at a temperature about 15°K . Three helium gas thermometers are connected by fine copper tubing to manometers conveniently located outside the liquefier. Two thermometers serve to indicate the level of the liquid hydrogen about P_3 and the third indicates the progress of the expansion at the valve M .

The liquid hydrogen is drawn in, in measured amounts, from a secondary reservoir through the valve C_1 . The hydrogen is pumped back to the gasometer, repurified to remove any impurities that may have entered due to the reduced pressure, and stored in cylinders for future use.

The liquid helium is collected in the flask F_1 and then siphoned

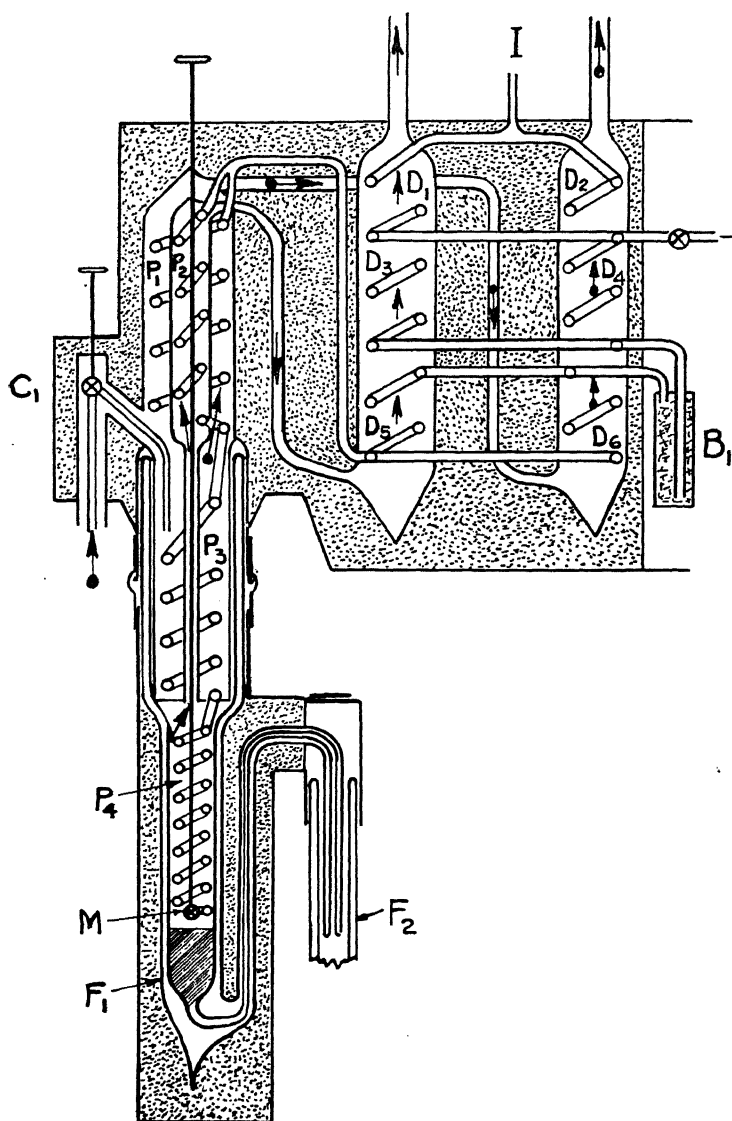


FIG. 7. Helium Liquefier

over to the flask F_2 intermittently. F_2 may contain the experimental equipment or may be used as a transport vessel to carry the liquid to the experiment. Cryostats for the use of liquid hydrogen and liquid helium are described in many publications.¹⁹

13. Liquid Helium—Simon Method^{20, 21, 22}

A discontinuous process for liquefying helium has been carried out by Simon and Mendelssohn and is useful for preparing small quantities of liquid helium at a relatively small cost; such an apparatus has been recently installed at Oxford University.

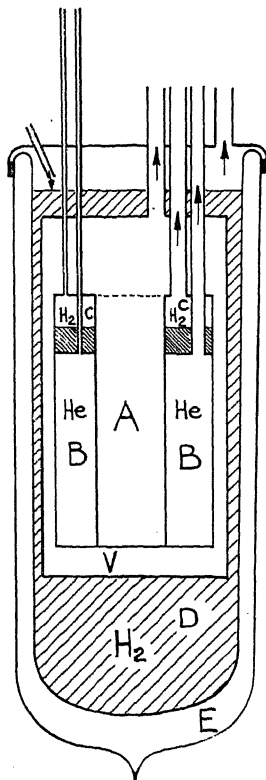


FIG. 8. Showing Apparatus of Simon and Mendelssohn

The method shown in figure 8 consists in the compression of helium to about 150 atmospheres in an annular space *B*, between two concentric cylinders. The inner cylinder *A* contains the experimental material. The cylinders are held in a metal container *V*, that is immersed in liquid hydrogen boiling at reduced pressure in *D*. The container *V* is at first filled with gaseous hydrogen or helium, in order to provide a conducting layer to bring the inner cylinders containing compressed helium to a temperature about 15°K. Additional cooling is provided by liquid hydrogen boiling under reduced pressure in the annular chamber *C*. The container *V* is then evacuated with a mercury diffusion pump and the compressed helium is allowed to expand. About half of it liquefies and serves to bring the two cylinders and the apparatus contained in *A* to the temperature of liquid helium.

An alternative process is to fill a separate container (not shown) in the chamber *B*, with charcoal or some other absorbing material and allow it to absorb helium, the heat of absorption being given off to the hydrogen bath. The chambers *A* and *B* are isolated as before from the liquid hydrogen bath and the absorbed helium is pumped off the charcoal. The lowering of temperature thus obtained liquefies a part of the helium in *B*.

The method succeeds because of the low heat capacity of solids at very low temperatures. Temperatures lower than 4°K are obtained by reducing the pressure over the liquid helium.

14. Down to a Temperature of 0.085°K

A method has recently been used for reaching still lower temperatures than have been available up to the present with liquid helium boiling at reduced pressures.

It was pointed out by Debye²³ and by Giauque²⁴ in 1926 that the temperature must decrease when a magnetized body is demagnetized adiabatically. Giauque and Clark²⁵ suggested that extremely low temperatures might be obtained in this way.

Recently de Haas, Wiersma, and Kramers²⁶, working at Leiden, performed experiments to test the method. The apparatus used is shown in figure 9.

The sample of paramagnetic salt S to be magnetized and demagnetized is contained in a small tube B within a small Dewar flask; the whole is suspended from a rod A which is attached to one arm of a balance (not shown in the figure). The whole apparatus is placed between the poles of an electromagnet M , in such a way that the salt occupies the region of maximum $H \cdot dH/dz$, z being the vertical coordinate. The suspended vessel is surrounded

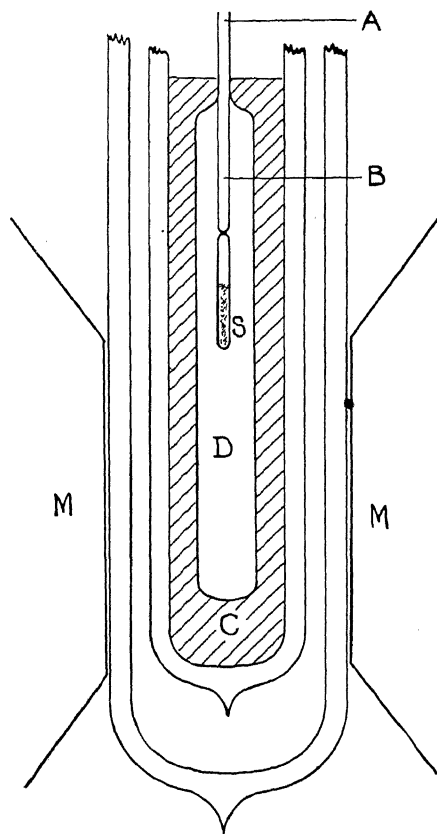


FIG. 9. Showing Apparatus used by de Haas to Produce the Lowest Temperatures by Demagnetization of Salts

(2) The effect of superimposing H.F. currents on direct currents while measuring D.C. resistance is to lower the transition or critical point for the sample. To show this effect the temperature was lowered until the D.C. resistance disappeared completely. High frequency current was then turned through the sample, the frequency was kept constant, and the value of the H.F. current necessary to bring the D.C. resistance back to its half-value was determined. Currents of two frequencies, *viz.* 60 cycles per sec. and 3×10^6 cycles per sec., were successively used on the same sample through which was being passed the same direct current, with the following results:

3×10^6 cycles per sec. (wave-length 100 m.)—140 m.a.

60 cycles per sec. (wave-length 5×10^4 m.)—230 m.a.

That is, the values of the alternating currents have the ratio of 2 to 3 while the frequencies change in the ratio of 50,000 to 1.

Silsbee and his co-workers,⁵² using small coils made of tin foil strips 0.02×0.0025 cm., superimposed a direct current of 6 m.a. on a radio-frequency current (1410 kilocycles per sec.) of 36 m.a. They measured simultaneously the direct current potential drop on a Wenner potentiometer and the variation in the radio-frequency current by means of a thermic milliammeter; they found that the discontinuity in resistance appeared simultaneously on both instruments.

It may be concluded that there is no appreciable change in the transition point as between direct and alternating currents for frequencies up to 3×10^7 cycles per second. The apparent change is indirectly due to the change in current distribution in the wire and probably directly due to surface changes of the conductor. Further, the effects of alternating current on the direct current resistance are probably due to magnetic fields, and certainly depend only on the magnitude of the high frequency currents.

CHAPTER III

ELECTRICAL RESISTANCE

15. Definition of Resistance

The electric current in a conductor is the quantity of charge passing any section of the conductor in a second; but the charge, consisting of ions and electrons, is incapable of direct observation, and we use the magnetic field due to the current as the measure of the latter. The unit current is the ampere which, while capable of theoretical definition in terms of the magnetic field, is at the present time practically defined as that steady current which deposits in a properly arranged apparatus 1.118 mg. of silver per second from a solution of a silver salt. The unit charge, the coulomb, is then the charge on 1.118 mg. of silver ion.

To keep a steady current flowing in a conductor, an electrostatic potential difference must be maintained across it, and for a large class of conducting materials, *e.g.* metallic wires, we find exact proportionality of the potential difference to the current flowing. This fundamental law of current electricity is known as Ohm's law (1825). It may be written: $E/I = \text{a constant}$, where E is the difference of potential between the ends of a wire and I is the current flowing through the wire. The constant of the above expression is called the resistance (R) of the conductor and, consequently, we have the ordinary expression: $R = E/I$. Consideration of the fundamental measurement of difference of potential gives at once the relation between the energy dissipated in the form of heat and the current flowing through the conductor. The difference of potential E between two points of a conductor means that E units of work are done when one unit of quantity of electricity is taken from end to end along this conductor. The work done per second with a current I is, therefore, given by EI ; this is the value of the heat developed in the conductor. We may write:

heat loss per second $=EI=RI^2$. Even if the electrical current is doing useful work such as running a motor or decomposing a compound substance, this amount of energy, RI^2 ergs, is always lost each second as heat.

In view of the definition of resistance for alternating currents, which will be dealt with later, it is useful to use this relation as a basis for a definition of resistance, thus: the resistance of a conductor is that quantity which, when multiplied by the square of the current, gives the energy (in this case heat) dissipated per second in the conductor.

It can be simply proved experimentally that for a series of uniform solid conductors, the resistance always varies directly as the length of the conductor and inversely as the area of its cross-section; or as expressed symbolically: $R \propto l/A$ or $R = s.l/A$, where s is a constant. This constant s , which has a specific value for each substance, is known as the specific resistance (or resistivity) and its reciprocal, usually written k , is known as the specific conductivity of the material.

A simple mechanical interpretation of Ohm's law can be given. If the density of mobile charged particles in a conductor does not depend on the current, the current can be increased only by increasing the rate of transport of these charges along the conductor, and the current will be proportional to the velocity imparted to the charged particles. Now if the mechanical resistance to the motion of the charged particles is proportional to the speed with which they move, the velocity of the particles will attain a terminal value proportional to the impressed force, *i.e.* to the fall of potential. Thus the current is proportional to the applied potential difference—the exact analogue of velocity proportional to force in the slow motion of a mass-particle in a viscous fluid.

The first attempt to produce a standard of resistance was made about 1846, when an arbitrary length of copper wire was selected and copies made from it. The permanence and reproducibility of such a standard leave much to be desired, and the modern standards have their prototype in the mercury standard of Siemens (1860). Theoretically the unit of potential difference, the volt, and the unit of current, the ampere, are independently defined, and it is

convenient that the unit of resistance, the ohm, be such that

$$E \text{ (volts)} = R \text{ (ohms)} \times I \text{ (amperes)}.$$

The international unit of resistance (the international ohm) is defined to satisfy this relation within the limits of accuracy of most measurements: it is the resistance at 0°C of a column of mercury of length 106.3 cm. and of the uniform cross-section necessary to give a total mass of mercury of 14.4521 gm. This standard is used to give a practical definition of the volt, namely the potential difference necessary to send 1 ampere (defined electrochemically) through a conductor of resistance 1 ohm. The mercury standard is exactly reproducible but is too cumbersome for use outside of standardizing laboratories. Copies constructed of metal wire, especially of manganin, are therefore made for general use. The wire is usually wound non-inductively and mounted in the familiar resistance box.

16. Variation of Resistance with Temperature

The resistivities of metals and alloys have formed the subject of many series of measurements. The values obtained depend on previous thermal and mechanical treatment of the specimens and on the temperature. The historical factor in particular makes most measurements of resistivity of an entirely illusory accuracy; for pure metals two significant figures alone are generally permissible, for alloys often only one. The study of the electrical properties of single crystals of metals avoids some of the difficulties due to an incomplete account of previous treatment.

The resistance of many pure metals²⁷ increases almost linearly with the temperature (figures 10 and 11). When the temperature is raised from 0° to 1°C the resistance of most metals increases by about 0.4 per cent. Mercury is the only striking exception, the increase being less than 0.1 per cent. The fractional increase of resistance at 0°C for 1° rise in temperature is close to the fractional increase in the volume of a gas at 0°C for a rise of 1° at constant pressure, and we may conclude that at ordinary temperatures the resistance is very nearly proportional to the absolute temperature. This rule is found to be roughly correct even at the low

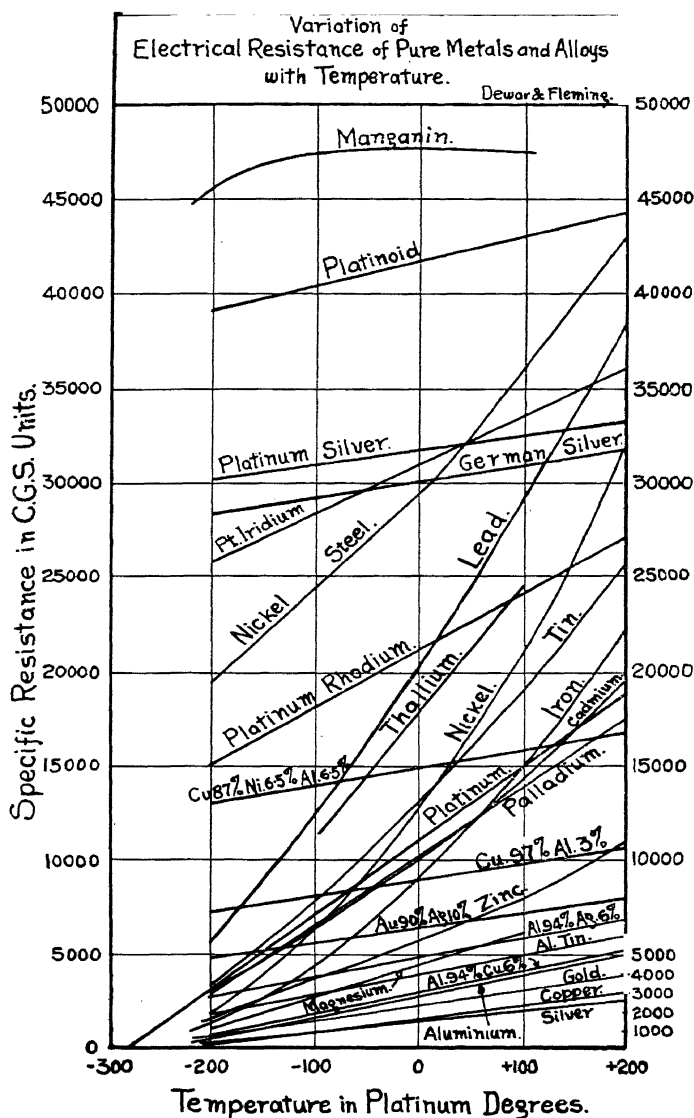


FIG. 10

temperatures of liquefied gases and the indications are that, as the temperature approaches the absolute zero, the resistance will practically vanish. Experiments of Kamerlingh Onnes²⁸ do, indeed, show that the resistance of metals becomes extremely small within a few degrees of the absolute zero, but the dependence on temperature ceases to be even approximately linear.

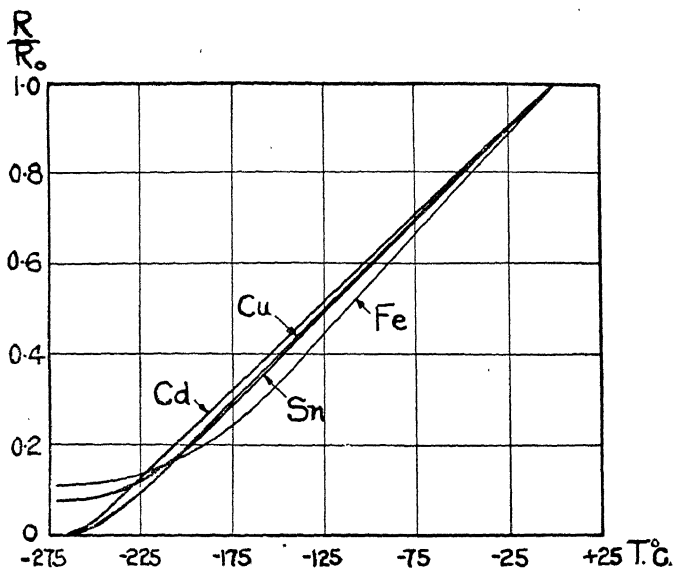


FIG. 11. Showing the Relation between Resistance of Metals and Temperature

R = Resistance at any given Temperature

R_0 = Resistance at 0°C

Quite distinct from this normal behaviour of resistance at low temperatures, a few metals and alloys show the phenomenon of superconductivity. For these the resistance abruptly drops to zero at a temperature characteristic of the metal or alloy.

A remarkable law was found in 1853 by Wiedemann and Franz,²⁹ who showed that the ratio of the thermal conductivity to the electrical conductivity is roughly the same for all pure metals.

More recent experiments have shown that this simple relation ceases to hold at very low temperatures, but the law has proved a useful criterion for testing the various theories of electrical conductivity (chapter 7).

The resistance of alloys is not calculable by the simple "mixing rule" from the resistivities of the component metals. In fact, in many cases the resistivity of an alloy is very considerably greater than that of any of its components. As might be expected, alloys are especially sensitive to any thermal and mechanical treatment, and numbers expressing their resistivities are of doubtful value when applied to random specimens. An interesting characteristic of alloys is their relatively small change of resistance with temperature (see figure 10); certain alloys, especially manganin, are so favourable in this respect that they may be used as resistance standards with little regard for varying temperature. In spite of this, however, some alloys become superconducting at very low temperatures.

Apart from metals and alloys, there is another class of conductors for which Ohm's law holds very accurately. This is the class of electrolytes, the conductivity measurements on which constitute some of the most precise physical data. The best conducting salt solution which can be formed has a resistivity about a million times greater than that of a good conducting metal.

On account of the fundamental importance of Ohm's law in precision measurements of electrical and magnetic quantities, great interest attaches to investigations of its accuracy, especially with conductors carrying heavy currents. Maxwell³⁰ and others, working as a committee of the British Association (1876), found no limitations to the law, and so great was the accuracy of their measurements that it is only within the last twenty-five years that their experiments have been repeated. After several investigators had failed to detect any deviations, Bridgman (1922)³¹ showed that, with current densities of several million amperes per square centimetre of the conductor, the resistance actually increases slightly with the current. For electrolytes carrying heavy currents, Wien (1927-9)³² detected small deviations from Ohm's law; in this case the resistance decreases slightly as the current increases.

CHAPTER IV

THE SUPERCONDUCTING ELEMENTS, ALLOYS, AND COMPOUNDS

17. Superconducting Pure Metals

Superconductivity is a phenomenon which appears at very low temperatures in a few metals, a large number of alloys, and several metallic compounds. The phenomenon consists of a sudden and, so far as can be determined experimentally, complete disappearance of electrical resistance as the temperature of the substance approaches the absolute zero. Since the absolute zero of temperature cannot be attained and the lower limit for purposes of measurement is at present in the neighbourhood of 1°K, it is impossible to say whether this property of perfect conduction is inherent in all metals or whether it is limited to those already known.

Mercury was the first substance to be shown to have this property. The discovery was made by Onnes (1911) who described it in the following words:³³ "The value of the mercury resistance used was 172.7 ohms in the liquid condition at 0°C; extrapolation from the melting point to 0°C by means of the temperature coefficient of solid mercury gives a resistance corresponding to this of 39.7 ohms in the solid state. At 4.3°K this had sunk to 0.084 ohms, that is to 0.0021 times the resistance which the solid mercury would have at 0°C. At 3°K the resistance was found to have fallen below 3×10^{-6} ohms, that is to one ten-millionth of the value which it would have at 0°C. As the temperature sank further to 1.5°K this value remained the upper limit of the resistance. [This value was probably the limit of small resistance which Onnes could measure.] The next step was obviously to look for the point at which the resistance first becomes measurable as the temperature is raised. The temperature of this point was found

to be slightly more than 4.2°K at which the resistance was found to be 230×10^{-6} or a hundred-thousandth of the resistance (solid) at 0°C . As the temperature was raised to that of the boiling point (4.3°K) the resistance rose once more to 0.084 ohms."

Onnes gave the name superconductivity* to this phenomenon. His curve representing the results for mercury is shown in figure 12. The feature which points to superconductivity in a substance is

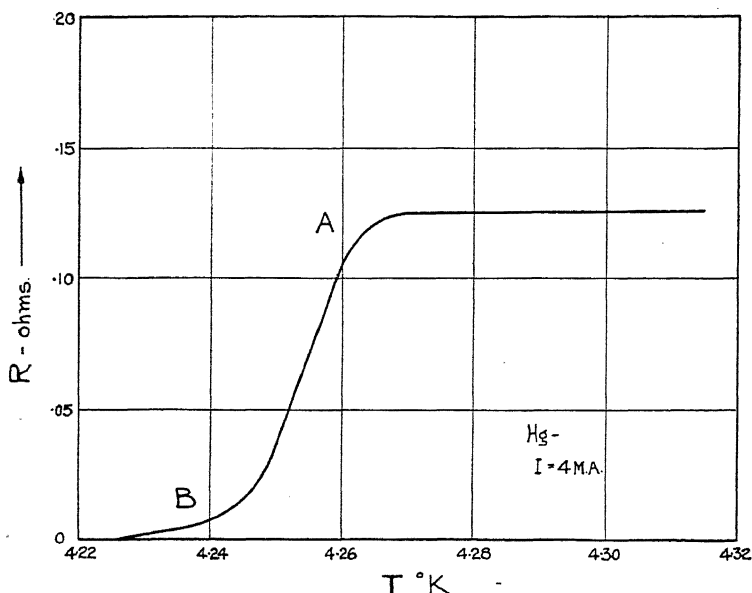


FIG. 12. Onnes's Curve for Mercury

the existence of a discontinuity in the resistance curve, *e.g.* at *A*, at which temperature the resistance starts to fall to an immeasurably small value. The term discontinuity is not used in its mathematical sense, but merely indicates a sudden and abrupt change in the slope of the curve.

*This word is sometimes written "supraconductivity", but after discussing the matter with many literary authorities the authors have decided in favour of "superconductivity".

At the same time as he was experimenting with mercury, Onnes determined the variation of the resistance of gold with temperature and found that its resistance fell gradually to an immeasurably small value, but that, unlike mercury, the gold resistance showed no discontinuity of the above type. As a consequence gold is not regarded as superconducting.

The initial point of the discontinuity A , which marks the commencement of the sudden loss of resistance, is called either the superconducting temperature or the transition point.* There is always a certain range of temperature between the point A and the point B over which the resistance, though falling rapidly, remains finite; this temperature interval is called the transition interval.

In much of the literature the resistance at low temperature is expressed as the fraction R/R_0 , where R_0 is the actual resistance of the sample at 0°C . At times, the fraction R/R_0 (where R equals the value at the transition point) has been called the residual resistance; at others, the resistance fraction or resistance ratio. In the present book, we shall define these terms as follows: residual resistance is the name given to the resistance at the superconducting temperature A , and the fraction R/R_0 will be known as the resistance ratio, R being the resistance at any low temperature.

TABLE OF SUPERCONDUCTING PURE METALS

Metal	Transition Point	Crystal Structure
Mercury.....	4.22°K	Rhombohedral
Tin.....	3.71	Tetragonal
Lead.....	7.2	Face-centred cubic
Thallium.....	2.37	Hexagonal
Indium.....	3.37	Tetragonal
Gallium.....	1.05	Tetragonal
Tantalum.....	4.4	Body-centred cubic
Thorium.....	1.5	Face-centred cubic
Titanium.....	1.75	Hexagonal
Niobium.....	9.2	Body-centred cubic
Aluminium.....	1.14	Face-centred cubic

*In some work relating to the effects of a magnetic field on the superconducting temperature, the term transition temperature is taken to mean the temperature at which the resistance of the sample comes back to a value equal to one-half the residual resistance after being cooled to a temperature below B .

It is, of course, apparent that the curve in figure 12 may be looked upon as showing the relation between the temperature T , and either R or R/R_0 , since R_0 is merely a constant.

Onnes³⁴ carried his investigations to other metals and found that tin, lead, indium, and thallium become superconducting. Since that time six other metals have been added to the list by de Haas³⁵ and Meissner.³⁶ The superconducting points and crystal structure of the superconducting metals are given in the accompanying table.

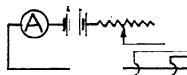
All the other pure metals tested have been found to maintain their normal variation of electrical resistance down to a temperature somewhat less than 1°K .*

18. Measurement of Superconducting Temperature or Transition Point

The measurement of the direct current resistance of a superconducting material involves the accurate observation of the changes in resistance which occur in the material as the temperature is decreased from just above the transition point. For most superconductors the residual resistance is small in comparison with the resistance at ordinary temperatures. In the case of mercury, the resistance at the transition point has a value of about .0005 of its value at 0°C ; this value, although small, is quite definite and measurable. As the temperature is lowered below this point, the resistance drops very rapidly to zero. In order to observe these small resistance changes, we must not only have a method suited to the measurement of low resistances but also one of the highest sensitivity. Among the various possible procedures, the potentiometer method is usually employed; the fall of potential so measured is independent of the long leads which must be run from the superconductor in the low temperature compartment to the measuring circuit. Figure 13 shows a schematic diagram of the arrangement. A constant current from the battery E is run through the specimen R_x . Current and potential leads are fastened to this specimen as shown. The voltage across it is observed in the potentiometer circuit, while the value of the current is determined by the ammeter A .

*See Appendix, p. 102.

Observations of resistance are limited by the sensitivity of the indicating galvanometer in the potentiometer circuit and, for reasons given below, by the magnitude of the current flowing through the specimen.



To Potentiometer:



FIG. 13. Showing Arrangement for Measuring Direct Current Resistance

An increase in the magnitude of the current sent through the specimen would give an increase of the potential fall to be measured and so would apparently increase the sensitivity of the potentiometer readings. However, there is a limit to the size of the current that can be used. Onnes found in his experiments with mercury and with films of tin that an increase in the current through the specimen tends to lower the transition point. This is shown by the curves³⁸ given in figure 14, which gives results obtained at Toronto for a tin-coated wire. This lowering of the superconducting temperature is thought to be due to the magnetic field set up by the current through the specimen, as the establishment of a magnetic field in the region about the specimen has the effect of lowering the transition point. The transition point is,

therefore, the temperature at which superconductivity sets in when the current through the specimen is small.

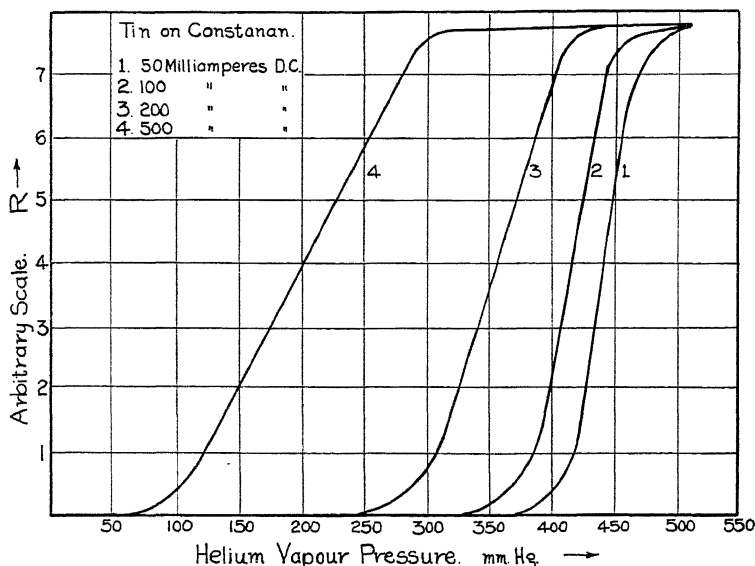


FIG. 14. Curves Showing Lowering of Transition Temperature with Increase in Current (100 m.m.=2.64°K, 250 m.m.=3.22°K, 500 m.m.=3.79°K)

19. Superconducting Alloys and Compounds

In the investigation of alloys, the phenomenon of superconductivity is found to be common to many; indeed, the number of alloys exhibiting the property is being continually increased. By far the greater number of superconducting alloys are binary alloys of which one or both components are superconductors. A few ternary and even quaternary alloys, particularly those of the type known as fusiole, are superconducting, and in these cases one or more components are superconductors. In fact, it is very probable that the mixture of any non-superconducting metal with a superconductor will produce a superconducting alloy, although the concentration of the non-superconductor may have

to be very small. In only one case, a gold-bismuth alloy, has a superconducting alloy been found in which both components are non-superconductors.

Among the metallic compounds several superconductors have been found. In these cases, also, the majority contain a superconducting element, as can be seen from the accompanying table. There are two carbides, however, those of tungsten and molybdenum, two nitrides, one sulphide, and one boride, which are superconducting although no superconducting element is present.^{30, 40, 41}

TABLE OF SUPERCONDUCTING ALLOYS AND METALLIC COMPOUNDS

Alloy	Transition Point	Compound	Transition Point
Sn-Bi	3.79°K	Bi ₅ Tl ₃	6.5°K
Sn-Zn	3.66	Sb ₂ Tl ₇	5.5
Sn-Sb	4.0	Na ₂ Pb ₈	7.2
Sn-Cd	3.62	Hg ₆ Tl ₇	3.8
Sn-Ca	3.6	Au ₂ Bi	1.84
Sn-As	4.0	CuS	1.6
Tl-Ag	2.65	VN	1.3
Tl-Cd	2.41	WC	2.8
Tl-Au	1.8	W ₂ C	2.05
Pb-Sb	6.6	MoC	7.7
Pb-Cd	7.2	Mo ₂ C	2.4
Pb-As	8.4	TiN	1.4
Pb-P	7.8	TiC	1.1
Pb-Ca	7.0	TaC	9.2
Pb-Li	7.2	NbC	10.1
Pb-Sn-Bi	8.5	ZrB	2.82
Pb-As-Bi	9.0	TaSi	4.2
Pb-Bi-Sb	8.9	PbS	4.1
Pb-Bi-Sb-As	9.0		
Pb-Bi-Sn-Cd	8.5		
Ti-Zr	1.3		

The general features of the superconductivity of alloys and compounds may be summed up in a few statements.

(a) Most alloys of which one component is a superconductor possess transition temperatures in the eutectic region the same as, or very little lower than, those of the pure superconducting metal. Examples of this type are Ag-Pb, Cd-Pb, and Sn-Zn.

(b) In one group of alloys, namely, those of bismuth, antimony, arsenic, and phosphorus with the superconductors lead, tin, and

thallium, the superconducting points of the alloys of the eutectic region are higher than those of the pure metals. There is one exception to this in the case of Pb-Sb where the transition point of the alloy, by weight 83 per cent. lead and 17 per cent. bismuth, is several tenths of a degree lower than that for pure lead.

(c) In an attempt to produce an alloy with a very high superconducting point, ternary and quaternary alloys containing lead and metals of the fifth group have been examined and found to become superconducting in the neighbourhood of 9°K.

(d) Among the superconducting compounds we find only one, Na_2Pb_5 , which possesses the same transition temperature as that of the pure superconductor.

(e) In the case of the nitrides, carbides, and borides, the transition temperatures are almost always higher than those of the pure superconductors. The most interesting example here is niobium carbide which becomes superconducting at 10.1°K, the highest transition temperature so far observed. It is quite possible, from indications observed in the transition curves for this carbide, that there may be other carbides of the metal with transition points as high as 12°K.

20. Relation of Constitution of Alloys and Transition Point

The earliest researches on the superconductivity of alloys were designed mainly to determine the extent of the phenomenon, and the alloys tested were usually in the eutectic region. Little attention was paid to the possible effect upon the phenomenon of varying the proportions of the components. Consequently, whereas the superconducting alloys and compounds now number about fifty, complete data on the effect of varying concentrations are known for only about a dozen alloy systems.

It was first shown by McLennan, Allen, and Wilhelm³⁹ that the superconducting point of an alloy is not independent of its composition. The various mixtures and compounds in the alloy systems Au-Pb, Ag-Sn, and Au-Sn were examined and it was found that each compound and mixture possesses its own characteristic transition temperature. It was then shown by Meissner⁴¹

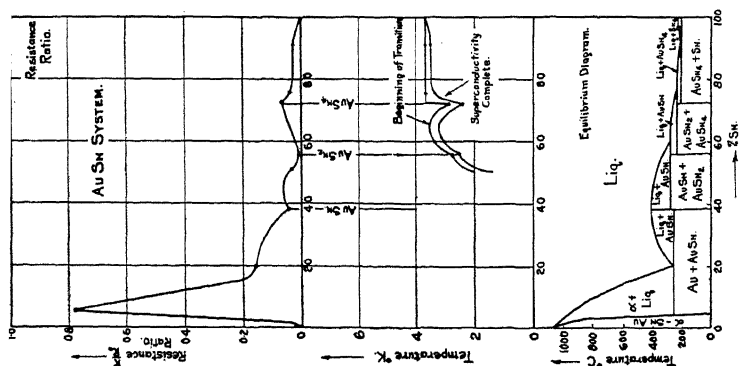


FIG. 15

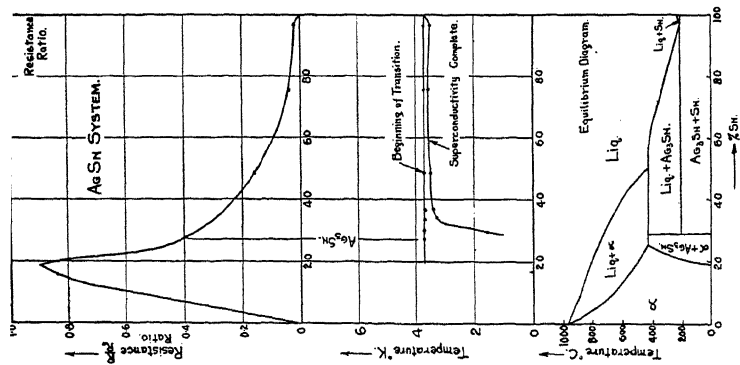


FIG. 16

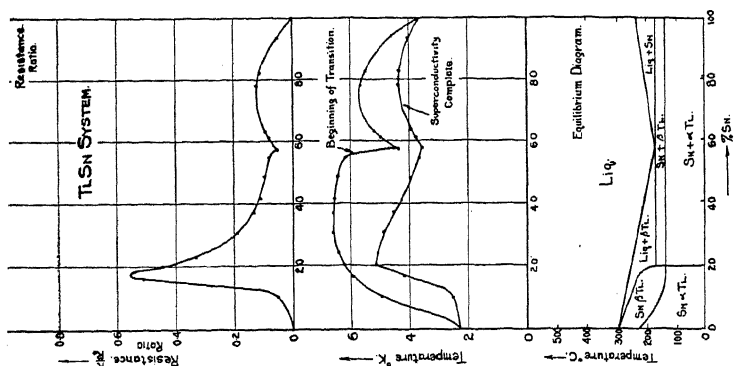


FIG. 17

Showing Relation between Resistance Ratios, Transition Points, and Composition of Alloys Au-Sn, Ag-Sn, and Tl-Sn

in an examination of the alloy systems In-Pb, In-Tl, Pb-Bi, Pb-Hg, Pb-Tl, Tl-Sn, and of other systems that the superconducting point of an alloy is a continuous function of the concentration. Recent research on the alloy systems Au-Sn, Au-Pb, Ag-Sn, Ag-Pb, Cu-Sn, Cu-Pb, and Tl-Sn confirm this.⁴⁴

Three typical examples of curves illustrating the relation between the composition of alloys and their electrical properties are shown in figures 15, 16, 17. These results cannot be taken as reproducible quantitatively, as the resistance of any alloy depends greatly on its previous history. The percentages are in each case by weight. As the laboratory at Toronto was not equipped at the time to produce temperatures below 1.88°K, readings cannot be given below that point.

Each of figures 15, 16, and 17 consists of three sections: (a) that showing the resistance ratio R/R_0 , plotted against the percentage composition; (b) curves showing the variation of the temperature of the transition point with the composition and also the relation between the end-point of transition and the composition; and (c) the equilibrium diagram of the given alloy.⁴²

Figure 15 gives details for the results of the gold-tin system; according to Vogel,⁴³ this system involves the compounds Au-Sn, Au-Sn₂, and Au-Sn₄, and the figures indicate definite transition point minima for the two latter compounds.

Figure 16 refers to the system silver-tin.

Figure 17 contains the corresponding information for the system thallium-tin. Remarkable results are evident in the eutectic region; both the transition point and the transition interval become a minimum at the eutectic. The transition interval increases from zero for pure tin to 1.3° for 78 per cent. tin, and then decreases to 0.8° at the eutectic. The interval grows to 2.5° again near 40 per cent. tin and again shrinks to 1.2° as the region of solid solution is approached. X-ray examination of these Tl-Sn alloys shows that both the components possess maximum lattice dimensions at the eutectic, showing a close relation between superconductivity and crystal structure.⁴⁴

The work of Meissner, de Haas and others⁴¹ and the X-ray measurements by Solomon and Morris-Jones⁴⁵ on the system

Pb-Bi, show a connection between the superconducting temperature and the dimensions of the crystal lattice. There are indications that the electrostatic field of force of the lattice is probably a fundamental factor in determining whether a substance will become superconducting or not.

21. Residual Resistance of Alloys

The residual resistance is more sensitive to structural changes than is superconductivity; it is also more dependent on structure and structural change than is specific resistance at normal temperature.

In spite of this sensitivity of residual resistance to structure, we can formulate several general statements concerning its behaviour in various types of alloy structures. The general conclusions regarding residual resistance are not unlike those arrived at concerning superconductivity.

(a) In simple eutectic regions, the residual resistance maintains a fairly constant value except in the neighbourhood of the boundaries of the region. Near the boundaries, the residual resistance increases towards a region of solid solution or drops sharply towards a pure metal boundary. The passage from one region to another on an equilibrium diagram is usually indicated in the residual resistance curve by a cusp-shaped maximum or minimum.

(b) In the case of solid solutions the variation and magnitude of residual resistance are greatest. Phases of this type show as well the greatest variation in other physical properties, such as hardness and tensile strength, which latter fact lends them industrial importance. The great variation in physical properties in solid solutions may be explained by the fact that the introduction of foreign atoms into a pure crystal induces lattice strains of considerable magnitude; these are responsible for great increases in strength, and in electrical and thermal resistance.

CHAPTER V

SUPERCONDUCTIVITY IN THE PRESENCE OF HIGH FREQUENCY ALTERNATING CURRENTS

22. Introduction to Experiments with High Frequency Currents

Work on the bearing of alternating currents on the phenomenon of superconductivity was initiated at Toronto in 1931 as a result of both experimental and theoretical considerations.

The existence of the superconducting temperature at once suggests that at this precise temperature some fundamental change must take place in the structure and properties of the metal specimen. Such changes might be expected to involve changes in the value of various constants of the metal, such as specific heat, expansion, and so on. Among the researches planned to discover such changes may be classed those of McLennan and co-workers⁴⁶ on (a) the absorption of β rays by superconductors at the transition point and (b) the photoelectric effect and light absorption of these metals at the transition temperature. In these experiments no measurable discontinuity was observed, as the metals were taken very gradually through the superconducting point. As these results deal with light frequencies, there does not appear to be a unique reaction at superconducting temperatures to electromagnetic fields alternating with a frequency as high as 10^{14} cycles per sec. It was argued thus: "It is clear, since superconductivity can be brought into evidence by the use of unidirectional fields, *i.e.* with fields of zero frequency, that there must exist some critical alternating field with a frequency between 0 and 10^{14} cycles per sec. by the use of which superconductivity should just be detectable".⁴⁷ Whether or not this reasoning is cogent, it did lead to testing the effect of high frequency currents on the superconducting points of various metals.

From a theoretical point of view, the abruptness of the onset of superconductivity recalls to the mind other striking phenomena involving similar discontinuity; for example, the piezo-electrical property possessed by quartz at ordinary temperatures suddenly disappears at a temperature of 580°C , and the Curie point of ferromagnetic substances involves a sudden crucial change in the molecular arrangement within the material. "Some of the theories put forward to explain superconductivity suggest that an orientation of some kind is involved in the production of the superconducting state in metals. If this suggestion should prove to be correct, one would expect some modification of the phenomenon for currents of high frequency. It need only be mentioned that all orientation effects are considerably modified in an oscillating field with a time-period of the order of, or less than, the time of relaxation of such orientation. A well-known example is that of the dielectric constant, which rapidly diminishes in value for very high-frequency electric fields. As to relaxation times, it will be recalled that in the case of ice, experimental evidence shows that the relaxation time is of the order of 10^{-6} sec. at 0°C and rapidly increases as the temperature is lowered. It would not seem unreasonable, then, to expect to find relaxation times exhibited by metals in the superconducting state, provided one used in one's experiment alternating fields of suitable and adequate frequencies."⁴⁷

23. The Meaning of Resistance with Alternating Currents

It has already been noted (§ 15) that, for direct currents, the resistance of a conductor, when the temperature is constant, depends only on the material and dimensions of the conductor. However, if the current is alternating, the above relation does not obtain, and it is necessary to enlarge our ideas of resistance. We have seen that from the relation—heat developed by direct current $= RI^2$ watts—the direct current resistance may be defined as that quantity which, when multiplied by the square of the current, gives the energy dissipated in the conductor—the energy dissipated being in the form of heat. When dealing with high frequency

currents, there are other ways in which energy is dissipated in addition to loss by heat. Consequently, the effective resistance for high frequency currents is always greater than the ohmic resistance and the additional energy loss is known to be due to a variety of causes. In the most general case, the effective resistance is defined as "that quantity which, when multiplied by the square of the effective value (or the mean-square) of the high frequency current, gives the energy dissipated in the conductor".⁴⁸ The important sources of this extra energy loss may be classified as follows: (a) currents induced in nearby conductors; (b) the so-called skin effect, due to the non-uniform distribution of current in the conductor; (c) conduction and dielectric losses in nearby insulators; and (d) parasitic condenser actions. The disturbances due to (c) and (d) can be minimized by careful design and manipulation of the conductor under test, but the effects of (a) and (b) always need to be taken into account.

24. Method of Inducing High Frequency Currents in Coils at Liquid Helium Temperatures⁴⁹

To obtain currents of a frequency of 10^7 cycles per sec. of measurable magnitude in any circuit, the latter should be resonant to the oscillations. In the experiments carried out the resonant circuit consisted of an inductive coil in series with a condenser, both being made entirely of the metal under test. This circuit was contained in a Dewar flask connected to the helium liquefier, so that the metal might be cooled below the superconducting point. The high-frequency currents were induced in the coil by a neighbouring oscillator (figures 18, 19).

25. Methods of Measuring Resistances with High Frequency Currents

(a) In order to measure the current induced in the resonant circuit submerged in the liquid helium, the reaction of this resonant circuit upon the generator of the oscillations, as indicated by the plate current of the latter, is determined. The frequency of the oscillator is varied on both sides of the natural frequency of the

resonant circuit, and values of the plate current are observed. The curve obtained with no coil present in the flask, but otherwise identical conditions, is subtracted from the curves obtained above. Resonance curves due to the coil at different temperatures are thus obtained, from which the high-frequency resistance of the metal is deduced.⁴⁹

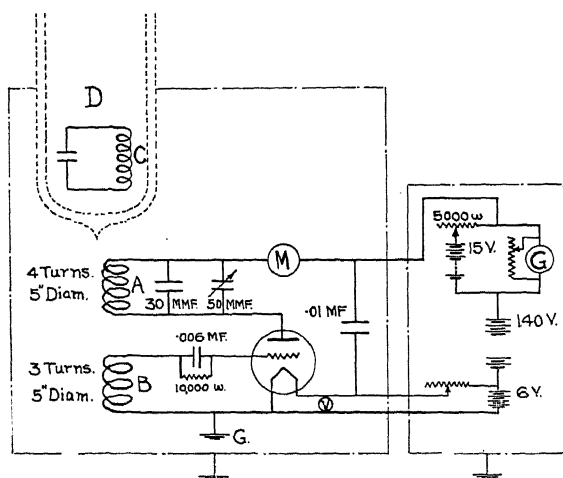


FIG. 18. Circuit Diagram Method *a*

The disposition of the resonant circuit in the flask of the helium liquefier is shown in the diagram (figure 18). The coil *C* of the pure metal under investigation is wound on a fibre form. The condenser is constructed of coaxial discs of the same metal separated by insulating spacers of small diameter. Helium gas or liquid from the liquefier can be circulated in the space *D* to bring the coil and condenser to the desired temperature, recorded by a suitable thermometer. The coils *A* and *B* of the oscillator are fixed on the axis of the coil about 8 centimetres below it. The number of plates on the condenser is adjusted until the fundamental resonance of the coil, when in position in the flask, is at the wave-length desired.

The oscillator, the circuit of which is given in figure 18, is of the tuned plate regenerative type, using a UX 112A vacuum tube. It is essential that, when the wave-length is varied over the range by the variable condenser across the plate coil *A*, there should be no abrupt or irregular changes in the intensity of the oscillations. To this end the resonance wave-length of the grid circuit is made much greater than that of the oscillations by using a large capacity for the grid condenser. It has been found that any form of choke in the circuit introduces parasitic oscillations, but by careful screening of the leads it is possible to dispense with its use.

In order that the value of the plate current may serve as an indication of the intensity of the oscillations, rectification by the grid condenser and leak method has been adopted as being more sensitive than the "anode bend" method, which is, perhaps, simpler. The total plate current is read by the milliammeter *M*, and small changes in its value are measured by the galvanometer *G*, the normal plate current through which is balanced by a potentiometer device. The oscillator is enclosed in an earthed copper screen and connected by screened leads to the batteries and galvanometer, which are contained in an earthed metal box. In this way, freedom from interference and from effects of body capacity is satisfactorily obtained. The voltage across the filament is kept at five volts for at least two hours to ensure steadiness before a trial is made. The variation in the plate current, Δi , is inversely proportional to the alternating current resistance of the resonator:

$$\Delta i = \frac{\text{constant}}{\sqrt{R^2 + \left(\omega L - \frac{1}{C\omega}\right)^2}}.$$

In case of resonance of generator and resonator:

$$\Delta i = \text{constant}/R$$

Consequently, when the resonant circuit becomes superconducting, there will be found an abrupt change of the plate current.

This method requires that the specimen coil *C* be coupled quite tightly to the oscillator; it was considered that methods involving looser coupling would be advantageous. This led to the use of three variations of the general method.⁵⁰

(b) The schematic diagram of this method is shown in figure 19. This is particularly satisfactory when used with samples which have a low resistance, *e.g.* solid tin wires. The resonant circuit was made up of the specimen under test, and a vacuum tube volt-meter was used to measure the voltage across a condenser in this

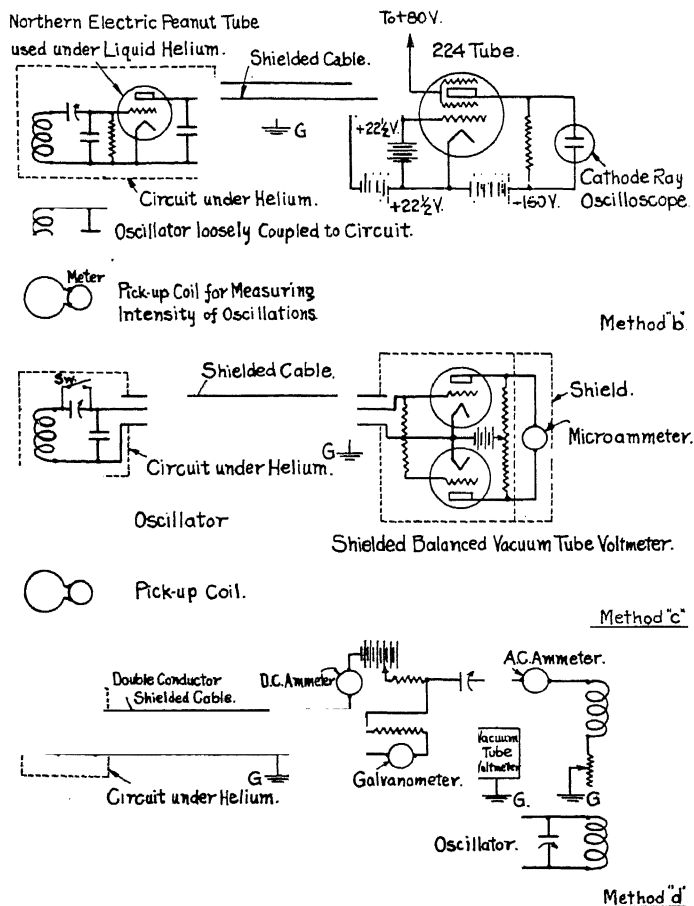


FIG. 19

resonance circuit. The vacuum tube used in the voltmeter circuit was of a miniature type so that it could be attached closely to the resonance circuit and lowered into the flask where it could be submerged in the liquid helium. Changes in the plate current in the voltmeter tube were amplified if necessary by the use of another tube outside the helium flask. In this method the output of the oscillator was kept constant and the current through the specimen read from the vacuum tube voltmeter.

(c) In figure 19c a balanced shielded detector circuit is shown. Using this method the output of the oscillator was varied to keep the current through the specimen constant.

(d) A fourth method, illustrated in figure 19d, while not as sensitive as the two preceding, was better for determining the effect of current strength on the resistance. It consisted in sending a measured alternating current through a concentric shielded cable to the coil under test. The voltage across a circuit consisting of a coil and a condenser of the correct capacity for resonance is then directly proportional to the sum of the resistances of the coil and the leads. Since the vacuum tube voltmeter is a "square-law" instrument, the sensitivity is increased by the presence of additional resistance in the leads, provided this is not too large. This is always less than the residual resistance of the coil. This method is the most satisfactory for measuring the effect of H.F. on the D.C. resistance and the effect of D.C. on the H.F. resistance. In measuring the latter effect, it is essential that the external resistance of the circuit be varied as little as possible, since any variation in this resistance will cause a variation in the apparent alternating current resistance of the sample. In the experiments voltages up to 720 volts D.C. were used to give a maximum current of 24 milliamps. The coil used was non-inductively wound and so designed that its resistance (just above the superconducting point) was not increased more than 10 per cent. by the direct current circuit.

26. The Effect of Neighbouring Conductors on the H. F. Resistance

The presence of nearby metallic conductors is always unavoidable since the experiments must always be performed close to

other apparatus. Such a nearby conducting body is equivalent in effect to the presence of a second circuit coupled to the primary conductor carrying the high frequency current under test, and will have with it a mutual inductance, say, M_s . Solution of the differential equations, which are very similar to those dealt with in the theory of the transformer, shows that this outside body has the effect both of lowering the reactance and of increasing the resistance of the primary conductor. If X_s , R_s are the reactance and resistance of the second circuit, then the reactance of the primary conductor is effectively *decreased* by $\frac{\omega^2 M_s^2 X_s}{X_s^2 + R_s^2}$, while the

resistance is *increased* by $\frac{\omega^2 M_s^2 R_s}{X_s^2 + R_s^2}$. The latter quantity we may

call the induced resistance and the observation of the resistance of the primary conductor then gives, not its ohmic resistance R , but the sum of R and the induced resistance. At very low temperatures, the ohmic resistance R may become very small compared to the induced resistance due to neighbouring conductors. Thus the difficulty of observing further decrease of the ohmic resistance R becomes much greater. If, as may be the case, the nearby conductor is very far from resonance with the oscillations in the primary conductor, then its reactance X_s , especially at low temperatures, will be much greater than its resistance R_s . In this case, the induced resistance to which it gives rise becomes approximately proportional to R_s . We see, then, that observations of the resistance of the primary conductor may depend upon the resistance of the nearby conducting material, especially if this material should vary in temperature during the experiment.

The existence of this additive induced resistance imposes a limitation on the use of the method, as the coil can never be very far from conducting material. Since the difficulties due to induced resistance increase with the frequency, the errors in such resistance measurements become greater at the higher frequencies. Even if the ohmic resistance in the superconducting state were really zero, the induced resistance would prevent an observation of the fact.

27. The Skin Effect in Relation to High Frequency Resistance Measurements

The other effect which is of major importance in the effective resistance of a conductor is the skin effect. By this is meant the tendency for the current to concentrate at the surface of a conductor when the current is alternating. The cause of this concentration of current may be understood by considering the magnetic field associated with the conductor when a steady current flows in it.

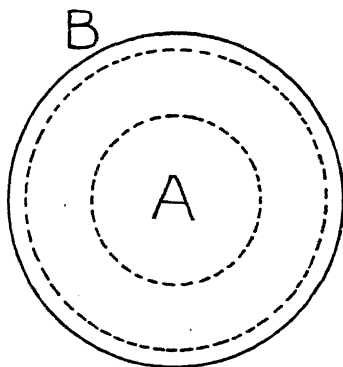


FIG. 20

If we take any cylindrical shell of a uniform circular wire, the magnetic field outside the shell is the same as if the same current were flowing along the axis of the conductor; however, inside the shell the field is zero. Thus the total magnetic flux is greater when the current flows along the axis than when it flows along the shell by the amount of flux which would exist in the shell space when the current flows along the axis. Thus two elements of a conductor each of equivalent cross-section, one at the axis *A* (figure 20) and the other *B*, at the surface, will carry equivalent *steady* currents, but the self-inductance of the axial element *A* will be greater than that of *B*. It is, then, evident that, if the current is alternating, the inner element of a conductor will have a greater impedance than the surface layer; thus the current density will tend to increase towards the surface.

Due to the greater inductance of the inner elements of a conductor, there is a phase variation in the current as one moves from the surface to the centre; indeed, there may exist a difference of 180° or more between the phase of the current at the surface and that at the centre. Thus any decrease in ohmic resistance of the central elements of a conductor will cause an increase in the total A.C. resistance of the conductor, since the current will be confined to a thinner shell. Obviously, an ideal conductor for high frequency resistance measurements of this type would consist of a thin tubular shell of high initial resistance (see § 29).

28. High Frequency Superconducting Temperature for Solid Metal Wires

The results of this phase of superconductivity have been reported in several papers from the Toronto laboratory.^{49, 50, 51} Observations have been made on lead, tin, and tantalum metals and a lead-bismuth alloy. In every case, the difference between results with H.F. and direct current is quite small; as a consequence, it is advantageous to work at a temperature at which the thermometric method is most sensitive. As temperatures below the boiling point of liquid helium (4.2°K) can be read easily to 1/100 of a degree, whereas, above that temperature, an accuracy of more than 1/10 of a degree is not easy to obtain, the choice is confined to such metals as tin and tantalum (see table, p. 50).

When using method (a) (§25) for measuring the high frequency resistance, there was indicated with each of the above metals at least a small drop in the transition point from that with direct currents, as indicated in the accompanying table:

Metal or Alloy	Transition Point for D.C.	Transition Point for High Frequency	Cycles per sec.
Lead.....	7.2°K	7.0°K	1.16×10^7
Pb-Bi alloy.....	8.2°K	(?) 8.2°K	1.16
Tin.....	3.77°K	3.68°K	0.645
		3.665°K	1.12
		3.65°K	1.61
Tantalum.....	4.41°K	4.28°K	1.16
		4.21°K	3.03

From the results with tin and tantalum, it was concluded that the transition point was lower the higher the frequency of the current, but this has not been entirely substantiated by later work.

Silsbee and his co-workers⁵² found that tin became superconducting for high frequency currents of 60, 2640, and 1,410,000 cycles per sec. respectively at the same temperature as for direct current.

In figure 21 are shown curves (2a, 2b) for the change in the H.F. resistance for currents of 5 and 70 m.a. (milliamperes)

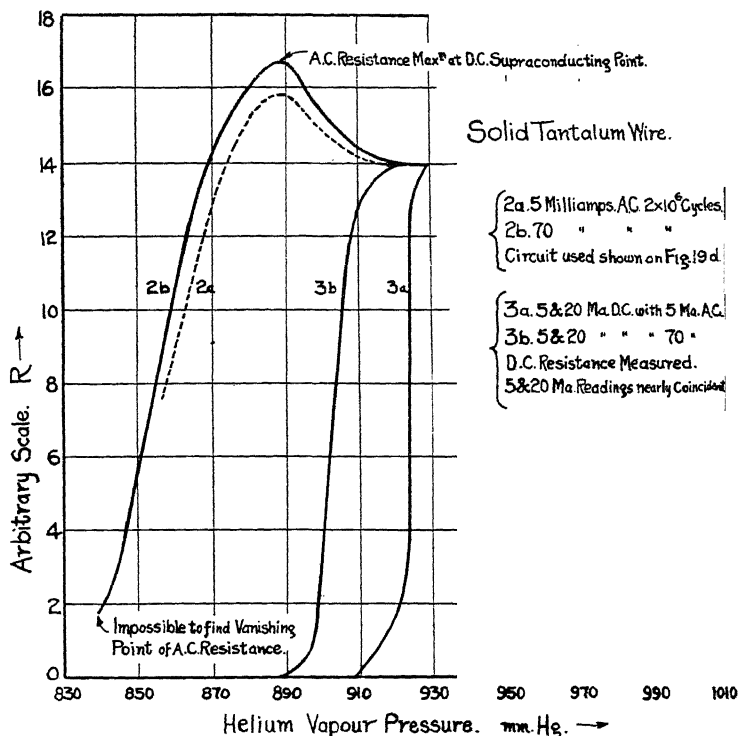


FIG. 21. Curves 2a and 2b Refer to Measurements of A.C. Resistance. Curves 3a and 3b Refer to D.C. Resistance when High Frequency Currents are Superimposed (§ 30) (760 m.m. = 4.22°K, 900 m.m. = 4.38°K)

respectively at a frequency 2×10^6 ; the D.C. resistance curve coincides closely with the curve *3a*, which can serve for comparison. The curve for 70 m.a. (*2b*) is more dependable than the one for 5 m.a. (*2a*), but the curves are almost coincident. Experiments carried out by the methods (figure *19b, c, d*), did not bear out the conclusion that the onset of temperature change came at a lower temperature as the frequency increased, but there were indications that the temperature at which the resistance reached its lowest measurable value became lower as the frequency increased. This latter point is rather indefinite because with the H.F. currents these methods never gave a resistance reading zero; this does not mean, of course, that the ohmic resistance may not really have attained the value zero.

Figure 21, *2a* and *2b*, contains a reproduction of the first results obtained with tantalum wire, the resistance being measured by method (*a*). The curious hump in the curves which was originally ascribed to experimental error is now believed to be a definitely reproducible phenomenon, observable with solid wires but not with thin films.

From what has been said with regard to the skin effect, it will be apparent that if the centre of the wire becomes superconducting while the resistance of a thin layer on the surface remains unchanged, then there may be observed an apparent rise in the effective resistance of the wire as a whole.⁵³

29. High Frequency Superconducting Temperature for Films of Metal

In order to overcome the difficulties involved by the unsymmetrical distribution of the current throughout a solid wire, thin films were attempted. This was accomplished by "wiping" a layer of block tin upon a constantan wire of diameter 0.016 cm. The thin film formed a cylinder of average thickness of about 0.002 mm.; as the constantan does not become superconducting, the result at low temperatures is that one has a thin cylinder of a superconducting metal on which to experiment. The presence of the tin on the constantan decreased the resistance of the con-

stantan wire at room temperature by about 7 per cent., and at a temperature just above the superconducting point of tin, the resistance of the constantan wire was about thirty times that of the tin.

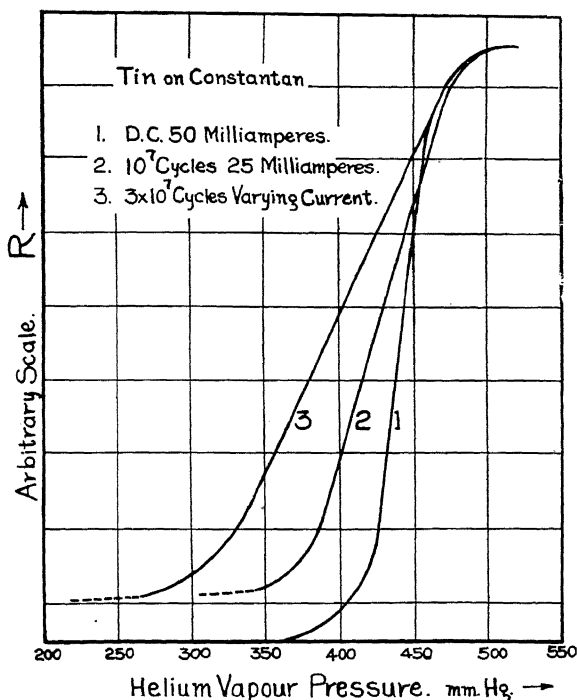


FIG. 22. Curve for Film of Tin on Constantan Wire
(250 m.m. = 3.22°K, 500 m.m. = 3.79°K)

In figure 22 are shown curves comparing the measurement of D.C. resistance (curve 1, current 50 m.a.) with the measurement for the same sample of the H.F. resistance at two different frequencies: curve 2, 10^7 cycles per sec., 25 m.a., and curve 3, 3×10^7 cycles per sec. and a current of varying value but always small. These measurements were carried out by using the method (c).

These results have three striking characteristics:

(a) The transition point is the same for D.C. and H.F. for small values of the current.

(b) The disappearance of the resistance or the vanishing point is at a lower temperature for H.F. resistance than for D.C. resistance; in fact, the value of the apparent resistance with the H.F. currents never became absolutely zero, as the D.C. resistance does.

(c) There was no indication of a slight rise in resistance before the sample becomes superconducting to H.F. currents, such as was invariably observed with solid wires (see figure 21, 2b).

30. The Effect of Superimposing Direct Current and Alternating Current

Experiments have been carried out in the Toronto laboratory with both solid wires and thin films of superconducting metal (tin) to determine (1) the influence of superimposing direct current on the H.F. current while measuring the H.F. resistance, and (2) the influence of superimposing H.F. current on the direct current while measuring the direct current resistance.

(a) *Results with solid wires*

(1) There is no appreciable effect on the transition point for H.F. resistance due to the superposition of a direct current for small values of the direct current.

(2) The influence of H.F. currents on the direct current resistance is illustrated in figure 21, 3a and 3b. The curves are coincident for direct currents of 5 m.a. and 20 m.a.; curve 3a shows the result of superimposing a H.F. current of 5 m.a. on these direct currents, while curve 3b is the result of superimposing 70 m.a. H.F. on the direct currents. The H.F. had a frequency of 2×10^6 cycles per sec. in each case. From these results we can conclude that the effect of H.F. currents on the D.C. resistance measurement is greater as the strength of the H.F. current increases.

(b) *Results with film (coated wire)*

(1) There is no appreciable effect on the transition point for H.F. resistance due to the superposition of a direct current for small values of the direct current.

(2) The effect of superimposing H.F. currents on direct currents while measuring D.C. resistance is to lower the transition or critical point for the sample. To show this effect the temperature was lowered until the D.C. resistance disappeared completely. High frequency current was then turned through the sample, the frequency was kept constant, and the value of the H.F. current necessary to bring the D.C. resistance back to its half-value was determined. Currents of two frequencies, *viz.* 60 cycles per sec. and 3×10^6 cycles per sec., were successively used on the same sample through which was being passed the same direct current, with the following results:

3×10^6 cycles per sec. (wave-length 100 m.)—140 m.a.

60 cycles per sec. (wave-length 5×10^4 m.)—230 m.a.

That is, the values of the alternating currents have the ratio of 2 to 3 while the frequencies change in the ratio of 50,000 to 1.

Silsbee and his co-workers,⁵² using small coils made of tin foil strips 0.02×0.0025 cm., superimposed a direct current of 6 m.a. on a radio-frequency current (1410 kilocycles per sec.) of 36 m.a. They measured simultaneously the direct current potential drop on a Wenner potentiometer and the variation in the radio-frequency current by means of a thermic milliammeter; they found that the discontinuity in resistance appeared simultaneously on both instruments.

It may be concluded that there is no appreciable change in the transition point as between direct and alternating currents for frequencies up to 3×10^7 cycles per second. The apparent change is indirectly due to the change in current distribution in the wire and probably directly due to surface changes of the conductor. Further, the effects of alternating current on the direct current resistance are probably due to magnetic fields, and certainly depend only on the magnitude of the high frequency currents.

CHAPTER VI

CHANGE IN PROPERTIES AT THE TRANSITION POINT

31. The Influence of Impurities on Transition Point of Metals

Since the time of the discovery of superconductivity, many theories have been put forward to explain the nature of the effect but, up to the present, no theory fits all the experimental data. The natural result of this continued research has been the acquisition of a considerable body of experimental knowledge of the physical properties of metals at low temperatures.

From careful measurements on the resistance of gold³³ at low temperatures, it was found that as the purity of the metal increases, the resistance remaining becomes less and less and seems to point to the fact that an ideal absolutely pure single crystal of gold would gradually approach a zero resistance value apparently attaining such value a few degrees above absolute zero. Kapitza⁵⁴ deduced from this that impurities in a superconducting metal maintained the residual resistance until the superconducting point was reached, at which point, for some reason, the impurities suddenly lost their resistance effect, and allowed the metal to become superconducting. That such was not the case was found by de Haas⁵⁵ in an investigation of single crystals of tin of utmost purity. It was found that increasing the purity and crystalline perfection of the metal resulted in a sharper transition from the normal to superconducting state. With as perfect a single crystal as de Haas was able to produce, the transition interval was approximately 1/1500th of a degree. It was concluded, therefore, that in an ideal superconducting metal, residual resistance still remained finite, and that the transition to the superconducting state was sharply discontinuous.

32. The Influence of Tension and Pressure on the Superconducting Point

A wire of tin subjected to mechanical tension was found to become superconducting at a temperature slightly above the normal point. This elevation of the transition temperature was proportional to the tension applied up to the point of fracture of the wire. The reverse process, that is, the application to a rod of tin of a compressional force, was found to produce a lowering of the superconducting point.⁵⁶

The effect of tension on the superconducting point was utilized by de Haas to explain the measurable transition interval of temperature always observed in the resistance-temperature curves for superconductors. Between the adjacent crystal faces of the normal polycrystalline metal, there must exist forces of some kind due to the assymetry present. Considering these forces as tensions, then along these faces superconductivity will appear at a higher temperature than it will through the body of the single crystals. Hence the resistance-temperature curve will commence to fall towards zero perhaps as much as several tenths of a degree above the point at which the metal is completely superconducting.

33. The Influence of a Magnetic Field on the Superconducting Point

The effect of an external magnetic field on a superconductor is the most marked, and perhaps the most important factor, other than temperature, to be considered in connection with superconductivity. Subjecting a metal to a magnetic field was found to produce a marked depression in the transition point.⁵⁷ The magnetic field delays the appearance of superconductivity, or if the field be strong enough, it will prevent the phenomenon from taking place altogether. If a metal, in the superconducting state and at a fixed temperature, is subjected to a gradually increasing magnetic field, a critical field strength is reached at which point the resistance suddenly reappears. The value of the critical field strength is independent of the relative direction of the field and the direction of the current in the metal; the only difference be-

tween fields of different directions is that a longitudinal field produces a larger residual resistance in the specimen than a transverse field.

If the field is then decreased below the value at which the resistance reappeared, the resistance remains constant, and only disappears again at a field strength considerably below the critical field. This phenomenon, which is called "resistance hysteresis", is analogous to supercooling, since for diminishing fields the resistance may disappear at any point below the critical field, and in practice it is

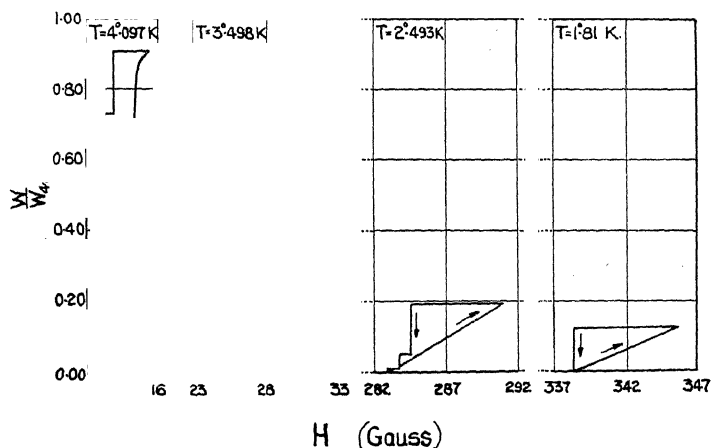


FIG. 23. Resistance Hysteresis Curves for Mercury (de Haas)

not likely to disappear twice at the same point. The resistance hysteresis loop is not in general formed of smooth curves as is the magnetic analogue. The section of the curve for increasing fields may be a smooth curve if the metal is composed of microcrystals, but even in this case the return curve for decreasing fields will be characterized by a great many small jumps or discontinuities. This is shown by the first curve of figure 23 which gives the resistance hysteresis curves as measured by de Haas⁵⁸ for a mercury resistance at four temperatures. The curves indicate that the values of the field at which the various crystals lose their resistance depend on the temperature in a way which is different for the different crystals.

At a given temperature the value of the magnetic field which restores the resistance of the metal to half the value of the residual resistance is known as the threshold value for that temperature. The relation between this threshold value and the temperature for a number of metals and alloys is shown in figure 24. The values for each substance are derived from a series of curves be-

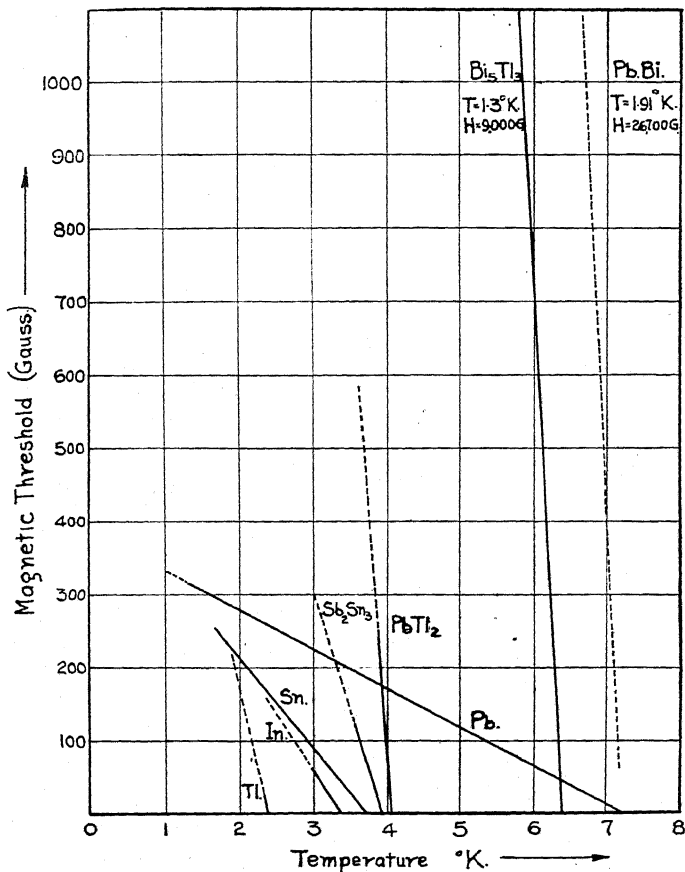


FIG. 24. Threshold Magnetic Fields for Various Metals and Alloys

tween resistance and magnetic field at different temperatures; an example of such a series is given in figure 25.

The current carried by a superconducting specimen produces a magnetic field which may be expected to affect the superconducting properties. A wire in the superconducting state will carry large currents without heating, and Onnes⁵⁹ was able to show that a finite resistance is restored when the current is raised

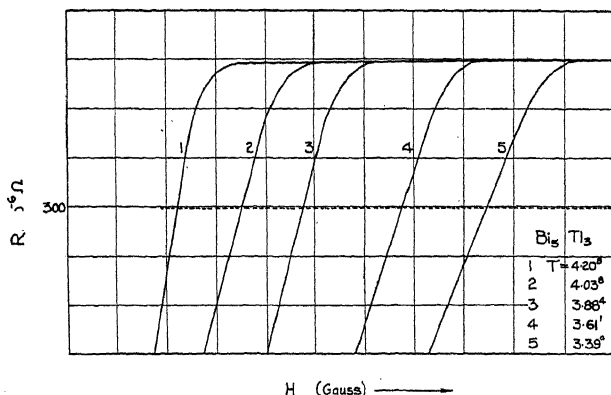


FIG. 25. Illustrating Method of Determining Values of Threshold Magnetic Fields

to several hundred amperes. Silsbee⁶⁰ showed that that current which restores the resistance of the specimen produces a magnetic field in the wire equal to the critical magnetic field for the substance.

34. Persistent Currents at Low Temperatures

A striking phenomenon, a corollary of superconductivity, was demonstrated by Onnes³⁷ shortly after he made his great discovery. If a current is started in any way in a closed circuit consisting of a superconducting metal kept at a temperature below its transition point, since there is no resistance in the circuit there will be no diminution in the current with time. If such a circuit, for example, a ring of lead, is placed in the helium flask supported in a magnetic

field and liquid helium introduced so as to cover the circuit, we have a conducting circuit at low temperature in a magnetic field. By destroying the magnetic field, a current will be induced in the ring and, since the resistance is zero, this induced current will continue to flow at a constant value. The current persists in the superconducting circuit so long as the metal is in the liquid helium. Measurements made on the time of decay³⁷ of such a current showed that this rate was less than 1/40,000 of its strength per hour, which was the limit of sensitivity of the measuring instruments used. Using this figure, we find by substitution in the equation,

$$i = i_0 e^{-Rt/L},$$

that the resistance of the superconducting ring must have been less than 10^{-12} ohm.

McLennan, Allen, and Wilhelm⁶¹ carried out experiments on the intensities of persistent currents of electricity induced in rings having the same dimensions and made of lead, tin, and tantalum respectively, brought into the superconducting state by the use of liquid helium. The currents in the rings were induced by the magnetic field provided by electric currents established in a circular coil of wire placed in turn coaxial with, and close to, each of the superconducting rings. The results of these experiments are represented by the graph shown in figure 26. It was found that, for the weaker magnetic fields, equal changes of flux produced currents of equal magnitude in each of the three superconductors. The magnitude of the persistent current developed depended not on the substance of the superconducting ring but only on its dimensions and on the magnitude and form of the magnetic field producing the induction.

The case of tin is very interesting, since the values of the current in it agree with those of the current in the others only up to fields of about 25 gauss. For inducing fields higher than this amount, the strength of the persistent current dropped off. Above this point, then, part of the ring must have been in a magnetic field, the strength of which had reached the critical value where resistance re-appeared, that is, an inner layer of the ring must have become non-superconducting. As the field was increased

above this point, one can suppose the outside superconductive portion of the ring became thinner and thinner until the whole ring became non-superconductive.

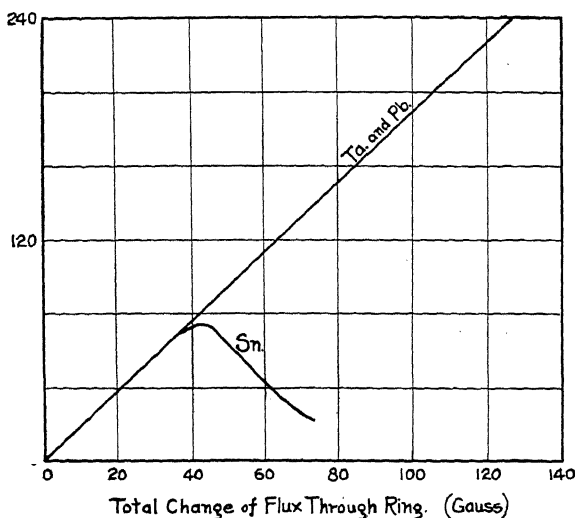


FIG. 26. Values of the Persistent Currents in Rings of Metal

The fact that the same flux engenders the same persistent current in different superconducting metals having the same size and form follows from an application of the equation

$$L \, di/dt = dB/dt \text{ or } i = B/L.$$

For rings of the same dimensions, the self-inductances would be identical; and in the superconducting state the resistances of the three metals would be vanishingly small. Self-induction and zero resistance were the two factors that made the magnitude of the induced current in different superconductors the same.

Looking at the matter in another way, we see that the induced currents in the three superconductors must be the same, since the magnetic field of the persistent current must be equal in magnitude and distribution but opposite in direction to the flux of the exciting field.

The dimensions of the rings were: 2 cms. outside diameter, 1.2 cms. inside diameter, and 0.4 cm. thickness. The strongest current developed in a ring was 240 amperes for a total change of flux of a little over 100 gauss. The highest current recorded was not the maximum possible since the critical field of lead at 2.0°K is about 500 gauss (see figure 24) which would produce a current through the ring of nearly 1000 amperes. Using a ring of Pb-Bi alloy, which has a critical field for restoration of resistance of 30,000 gauss at 1.2°K (figure 24), it should be possible with a total change of flux of that amount to produce a persistent current of over 50,000 amperes in a ring of the size given above.

35. Variations in Expansion at the Transition Point

It was at one time thought that perhaps superconductivity was the result of some allotropic modification which took place at the transition temperature. Although Keesom⁶² found no first order change in the crystal structure of lead as the metal passed the superconducting point, the question of an allotropic change is not entirely settled. Research is still being carried on to test for secondary changes in the crystal structure of the metal at the superconducting point.

An experiment was carried out by McLennan, Allen, and Wilhelm⁶³ on the thermal dilatation of superconductors. Two short lead rods were made to operate an optical lever. The rods were fixed to a quartz bar and the apparatus cooled by helium vapour to the liquefaction point of helium. No break in the thermal expansion curve was found at the superconducting point, which gave evidence that no great change in the crystal structure occurred at that point. The shape of the thermal expansion curves at low temperatures was similar for both pure lead and the superconductive fusible alloy Pb-Bi-Sn (Rose's metal). The most interesting and significant feature of the expansion curves was the difference in shape above and below the transition point. Above the superconducting point, the expansion curve seemed to follow a parabolic law with apex at the superconducting point, while below this temperature, the curve appeared to be straight or

nearly so and with only a minute contraction. These features can be clearly seen in figure 27.

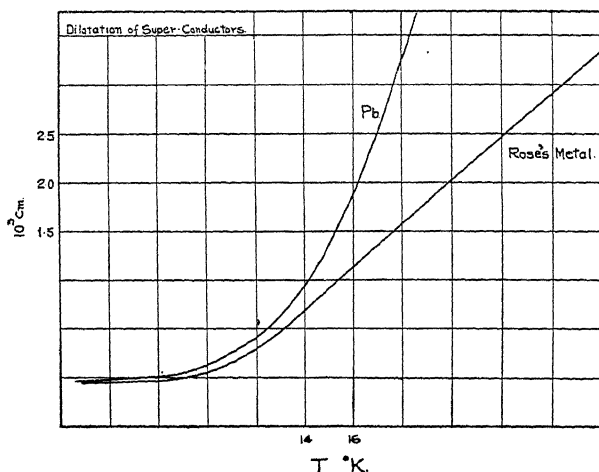


FIG. 27. Curves of Expansion of Superconductors at Low Temperatures

36. Variation in Specific Heat and Thermal Conductivity at the Transition Point

The evidence in favour of a secondary change in structure of the ionic lattice, or in favour of the solid superconducting electron lattice theory of Kronig,⁶⁴ is found in the results obtained from careful measurements of the specific heat of tin and the thermal conductivity of indium at low temperatures.⁶⁵ Both these properties were observed to undergo abrupt changes at the respective superconducting points. The specific heat of tin⁶⁶ (figure 28) was found to increase suddenly by some 20 per cent. at the transition point. Previous measurements on the specific heat of lead⁶⁶ showed no change at 7.2°K, but it is possible that the measurements were not sufficiently delicate to show a possible change. Indium was found to conduct heat much better immediately below the transition temperature than immediately above. These changes in thermal properties are what one would naturally expect if the

appearance of superconductivity was the result of the sudden solidification of an electron lattice. The other superconducting metals should also show these changes and it will be necessary to investigate them before pronouncing upon the theory.



FIG. 28. Variation of the Specific Heat of Tin at its Transition Temperature

37. Miscellaneous Variations at the Transition Point

Many other physical properties of metals have been examined in the superconducting region of temperature with usually negative results. The photo-electric effect,⁴⁶ the absorption of β particles,⁴⁶ the absorption of slow electrons,⁶⁷ and the torsion constant⁶⁸ all show no change in the transition to the superconducting state.

38. Summary of Changes at the Transition Point

Practically the whole range of physical properties of metals which it is experimentally possible to observe at low temperatures have been investigated in connection with superconductivity. We see, however, that there is only one great factor affecting superconductivity and that is magnetism. Other effects are secondary.

The chief properties other than electrical which are found to alter at the superconducting point are thermal in character, that is, specific heat and thermal conduction. It will probably be from these latter properties and from the magnetic effect that the explanation of the phenomena of superconductivity will arise.

CHAPTER VII

THEORIES OF THE SUPERCONDUCTING STATE

39. Electron Theories of Conduction

All theories of metallic conduction of heat and of electricity postulate the existence in metals of so-called conduction electrons. Since the beginning of the present century, attempts have been made to characterize this electron gas of a metal in such a way as to enable quantitative predictions of optical and electrical properties of the metal to be made. In the early work of Drude and Lorentz, the model of a metal is particularly simple: the conduction electrons move freely in the spaces between the heavy, fixed atoms of the metal, with which they exchange energy by collisions and so assist in the establishment of thermal equilibrium. The electrons are characterized as free, and, apart from the collisions with the atoms, behave as an ideal gas, their mutual interactions being neglected. In the language of the kinetic theory of gases, the mean free path of the electrons will be determined not by their mutual collisions which are infrequent, but by collisions with the metal atoms. A uniform distribution of electrons, realized in a metal in electrical and thermal equilibrium, will be disturbed by any electrostatic potential gradient which may be applied. The electric field, acting on the electrons while they traverse their free paths, will superpose on the isotropic equilibrium distribution a net flow in a direction which, with the usual conventions regarding signs, is opposite to the field. A simple calculation gives the magnitude of the current: with $I = \sigma E$, where I is the current density, E the field, and σ the electrical conductivity, Lorentz⁶⁹ found for σ the expression

$$(1) \quad \sigma = 2 \sqrt{\frac{2}{3\pi}} \frac{ne^2\lambda}{mv},$$

where n is the number of electrons per unit volume of the metal, e , m the electronic charge and mass, λ the mean free path of the electrons, and v their root-mean-square velocity. We may write

$$(2) \quad \sigma = \sqrt{\frac{2}{3\pi}} \frac{ne^2\lambda v}{\frac{1}{2}mv^2},$$

and replace the mean kinetic energy by $3kT/2$, the value ascribed to it by the classical kinetic theory:

$$(3) \quad \sigma = \frac{2}{3} \sqrt{\frac{2}{3\pi}} \frac{ne^2\lambda v}{kT}.$$

A temperature gradient in a metal will also cause an electron current which is easily calculable by the same principles. The coefficient of thermal conduction is found to be

$$(4) \quad \kappa = \frac{4}{3} \sqrt{\frac{2}{3\pi}} n\lambda vk,$$

and the ratio of κ to σ is given at once:

$$(5) \quad \frac{\kappa}{\sigma} = 2 \frac{k^2}{e^2} T,$$

the experimental law of Wiedemann and Franz (1853):²⁹ the ratio of thermal to electrical conductivity is the same for all metals at the same temperature. The derivation of this law represents one of the striking successes of the early form of the electron theory of metals, although the numerical coefficient involved is about 30 per cent. too small to be regarded as satisfactory from an experimental point of view.

Serious difficulties soon develop when the theoretical results are more closely inspected. If the free electrons are really amenable to the methods of the classical gas theory, they must be assigned their full share $3nkT/2$ of translational energy, and this would contribute a term $3nk/2$ to the specific heat (per unit volume) of the metal. As there are no systematic differences in order of magnitude of the specific heats of metals (with free electrons) and

of non-metals (presumably with few free electrons), one is compelled to assert that n must be small compared with the number of atoms per unit volume. But unless n is taken to be of the order of magnitude of the number of atoms per unit volume, it is impossible to get the right order of magnitude for κ and σ , unless, on the other hand, λ is assumed to be many thousand times the mean atomic separation.

The calculated dependence of σ on the absolute temperature can indeed be made, by fairly plausible arguments, to agree with experiments at high temperatures, but no assumptions can be devised to give agreement at low temperatures. At high temperatures σ is found experimentally to be roughly proportional to $1/T$, and this necessitates that the product $n\lambda v$ in (3) shall be independent of T . The assumption which J. J. Thomson⁷⁰ could not avoid in an effort to explain the Thomson effect is that n is proportional to \sqrt{T} , and since v is also proportional to \sqrt{T} we must have a mean free path varying inversely as the absolute temperature. Granting for a moment that this is the case, no possibility remains of accounting for the rapid fall of resistance at extremely low temperatures; a decrease proportional to T itself is quite insufficient. The low temperature region is, in fact, one of fundamental difficulty for the electron theory; even the Wiedemann-Franz law ceases to apply. The classical form of the electron theory is, moreover, useless to account for contact potentials and the familiar Volta sequence.

The failure of classical statistical theory to reproduce the correct radiation formula led, as is now well known, to the various postulates of the quantum theory, and it was not long before similar attempts were made to modify the treatment of the electron gas. Nernst and K. Onnes (1911)⁷¹ gave empirical formulae for the resistance of metals suggested directly by the form of the Planck radiation formula. Lindemann (1911)⁷² retained both the hypothesis of Thomson that n is proportional to \sqrt{T} , and the principle of equipartition, and endeavoured to account for a suitably varying free path λ by referring to the thermal agitation of the atoms. Although a reasonably good resistance formula can be so constructed, all the other difficulties of the Lorentz treatment remain. Wien (1913) ascribed to the electrons a velocity independent of the temperature,

and so removed their contribution to the specific heat of the metal. This again reduced the variation of resistance with temperature to a problem of a suitably varying free path. The latter problem was attacked by using the complete elastic spectrum of the metal atoms, familiar from the work of Debye on specific heats of solids. At low temperatures there is predicted a resistance varying as T^2 , but thermal conductivity and the Wiedemann-Franz relation cannot be accounted for, the electrons being unable to transport kinetic energy.

Lindemann (1915)⁷³ rejected the concept of a gas of free electrons and supposed that the electrons in a metal are so coupled as to constitute a lattice of considerable rigidity. This view, later developed by Borelius (1918)⁷⁴ and Haber (1919),⁷⁵ represents conduction by the motion of an electron lattice through the ionic lattice of the metal. If, in accordance with the Planck postulate, the energy of the lattice is quantized, the specific heat difficulty disappears; the small mass of the electrons ensures that the electron lattice vibrations will be of much higher frequency than the vibrations of the ionic lattice. The superconducting state of a metal will occur at temperatures where the thermal agitation of the ionic lattice has so far decreased as to offer no appreciable interference to the free motion of the electron lattice.

In a survey of the development of the electron theory up to about 1925, we notice the increasing disrepute of the electron gas concept. The lattice concept of Lindemann was probably never regarded, however, as providing an escape from the difficulties mentioned above. It gave only a few qualitative ideas and was unable to suggest any solution of its main difficulty, the existence and stability of the type of electron lattice postulated. We shall, however, have occasion to return to this view from a more recent standpoint.

Now the difficulties of the electron gas theory of metallic conduction are precisely those which occur in several other famous classical problems where the use of the Boltzmann statistical methods led to disagreement with observation. The modern developments of the quantum theory have led to the introduction into physics of two new systems of statistics. One of these, de-

veloped by Bose and by Einstein (1924), is apparently appropriate for dealing with radiation, for which the classical system leads to the untenable Rayleigh-Jeans law. The other system, due to Fermi and to Dirac (1926), is adapted to the treatment of electronic statistics, and was applied by Sommerfeld (1927) with considerable success to the electron gas in a metal. The two new statistical systems and the system of Boltzmann all give practically the same results when applied to a gas at high temperatures. But at low temperatures the quantum statistics lead to very different results from those obtained on a classical basis. A gas with particles of electronic mass will show, even at high temperatures, the degenerate behaviour of an ordinary gas near to the absolute zero.

Applying the Fermi statistics to the electron gas, a process involving only formal modifications in the original Lorentz method, Sommerfeld⁷⁶ derived for the electrical conductivity the expression

$$(6) \quad r = \frac{4\pi}{3} \frac{e^2 \lambda}{h} \left(\frac{3n}{4\pi} \right)^{2/3},$$

the only new quantity introduced here being the Planck constant h . At first sight the expression appears to make σ independent of T , and if n is to be regarded as at least approximately constant, the dependence on temperature must be introduced through the mean free path λ . The thermal conductivity is found to be

$$(7) \quad \kappa = \frac{4\pi^3}{9} \frac{\lambda k^2 T}{h} \left(\frac{3n}{4\pi} \right)^{2/3}$$

and the new expression for the Wiedemann-Franz law is

$$(8) \quad \frac{\kappa}{\sigma} = \frac{\pi^2}{3} \frac{k^2}{e^2} T.$$

The numerical factor $\pi^2/3$ instead of the Lorentz factor 2 in equation (5) is, indeed, in much better agreement with experiment. Moreover, the specific heat difficulty vanishes at once with the use of the new statistics (which does not give equipartition of energy). For the first time in the development of the electron theory, contact potentials and the Volta series are reasonably well predicted, and various phenomena such as the Thomson and Peltier

effects are, at least qualitatively, capable of explanation. The use of the new statistical system undoubtedly represented a great advance in the electron theory of metals. The weaknesses in the first developments of this view are again connected with the mean free path λ . This was regarded originally (though provisionally) as geometrically defined, but this deficiency in the theory was soon repaired by Houston,⁷⁷ Frenkel,⁷⁸ and others. It is not necessary now to give details of the modifications of the free-electron gas theory from this point of view, for it was almost immediately recognized that the whole model of a conducting metal had been over-simplified: the motion of the electrons cannot be regarded as occurring in a force-free space.

The next attempts to construct a more satisfactory electron theory of conduction were made by Frenkel⁷⁹ and by Bloch⁸⁰ on the basis of the wave mechanics. The behaviour of atoms or of electrons can be described in two mutually complementary ways, firstly by regarding them as corpuscles, and secondly by regarding them as waves. This statement, a rough presentation of the fundamental principle of duality in the modern quantum theory, will recall the more familiar dual nature of light, which in some phenomena evinces a corpuscular nature and in others a wave nature. If now the electrons in a metal are regarded as wave systems rather than as material particles, it becomes possible to treat the whole problem of conduction in a different manner. The electrons are still considered to be uncoupled, though the field in which any one electron moves is found by an averaging process over the other electrons. If no thermal agitation affects the metallic lattice through which the electrons move, that is, if the metal is at absolute zero, the lattice of the metal simply determines a periodic potential field for the electronic motions, and it is found at once that the electrical resistance offered by such an immobile lattice is zero. When, however, the metallic ions are thermally agitated and the potential field disturbed, the electrons experience a resistance, that is, an electron moving through the lattice loses energy to the ions of the metal. If the heat motions of the lattice are analysed into the corresponding elastic waves, we may describe the resistance as due to energy exchanges between these waves

and the electronic waves; or we may say that the electron waves are scattered by the elastic waves. At ordinary temperatures Bloch's theoretical treatment of the problem gives for the electrical conductivity an expression which does not differ appreciably from the simple result of Sommerfeld. At very low temperatures, however, a conductivity proportional to T^3 is found, in fair agreement with experiment which gives a proportionality between T^3 and T^4 for many metals.

40. Theories of Superconductivity

None of the above-mentioned theories of electronic conduction, either classical or quantum-mechanical, is capable of providing an explanation of the phenomenon of superconductivity. It appears that any statistical treatment of free electrons leads inevitably to a finite resistance at any finite temperature, however small. One therefore arrives at the conclusion that the failure to account for superconductivity lies, not in the character of the mathematical development, but rather in the neglect of some important feature of the metallic model which is chosen as the starting-point for the mathematical treatment.

It is probably impossible in the present state of knowledge of metallic crystals to account for many of the varied phenomena, such as the details of the superconductivity of alloys, and the various factors which affect the steepness of the transition. It is quite sufficient at present if a proposed theory can explain, besides the absence of resistance at very low temperatures, the following main experimental facts concerning the superconductivity of a single crystal of a pure metal:

(a) The sharpness of the transition to the superconducting state; in some cases the resistance falls from a value in fair agreement with the Bloch theory of conduction down to zero within a temperature range of less than a hundredth of a degree.

(b) The effect of a magnetic field in restoring the resistance; a specimen appears to lose its superconducting property suddenly under a certain critical magnetic field which depends upon the temperature.

(c) The disturbance of the superconducting state by high frequency currents.

(d) The absence of appreciable changes in the non-electrical properties of the metal, and especially the absence of an effect on the thermal conductivity analogous to the electrical superconductivity.

(e) If the basic hypothesis of the theory takes the form of a definite atomic model, it should also explain why the known pure superconductors are grouped in the central columns of the periodic table.

Benedicks' Theory. It would be beyond the scope of the present work to review in detail all the classical and semi-classical models which have been put forward from time to time in an attempt to account, at least qualitatively, for superconductivity. Mention should be made, however, of the theory proposed by Benedicks in 1915⁸¹ and recently revived.⁸² In this model, which was also considered by Bridgman⁸³ in connection with his work on the effect of high pressures on electrical resistance, conduction in general is ascribed neither to an electron gas nor to a lattice of coupled electrons, but to the passage of valence electrons from one atom to the next within the metallic lattice. As long as there is a finite separation between the outer electron orbits of neighbouring atoms, a resistance should exist, and should increase with the interatomic separation. It may be imagined, however, that for certain metals a point is reached with lowering of the temperature where these orbits come into tangential contact. This is the sharp superconducting point, for below this point it may be said that the radiationless, and, therefore, resistanceless, electron orbits form through the crystal lattice a continuous chain along which the electrons will move under the influence of an external field. Starting from this basis it is possible to explain qualitatively all the principal phenomena of superconductivity. For example, the effect of the magnetic field upon the transition point is explained very simply by consideration of the effect of the field upon the chain orbits.

Kronig's Electron Lattice Theory. In Bloch's theory of metallic conduction the view may be taken that the existence of electrical resistance is due to the electrons giving up to the metallic ions, by

collision, the kinetic energy they have acquired under the influence of the applied field. It was therefore suggested by Bartlett⁸⁴ that a crystal model in which the exchange of energy between the electrons and the ions was for some reason impossible would be superconducting. Two recent extensive treatments of the problem, those of Kronig⁸⁵ and Dorfman,⁸⁶ have followed this line with considerable success.

Kronig supposes the existence at absolute zero of a rigid electron lattice, formed within the metal independently of the ionic lattice of the metal itself. This may be supposed to maintain its rigidity for a few degrees above the absolute zero, so that Kronig's model amounts practically to a re-introduction of Lindemann's hypothesis as regards very low temperatures only.

For purposes of mathematical treatment the thermal motions in both the electron and ionic lattices may be analysed into systems of harmonic waves. These will be quantized so that only a negligible number of waves are excited for which $h\nu$ is much greater than kT . On account of the small mass of the electron, the velocity of these waves will be very much greater in the electron lattice than in the ionic lattice, and so at temperatures only a little above the absolute zero the shortest waves excited in the electron lattice will have wave-lengths many times longer than those of the ionic lattice. One may therefore neglect the thermal fluctuations of electron density and consider the electron distribution over a wave-length of the ionic lattice as given by the rigid electron lattice. The electrons in this lattice are then to be treated as subject to a small perturbation due to the displacement of the ions from their positions of equilibrium. This might be treated mathematically according to the usual methods of perturbation theory, but a simple consideration shows that the perturbation function, averaged over a finite volume of the metal, is zero. Therefore, as long as the electron lattice maintains its rigidity, it cannot give up energy to the ionic lattice, and it follows that there can be no electrical resistance.

For an explanation of superconductivity it still remains to be shown that it is possible for a current of considerable density to flow. It is conceivable, for example, that such a model might be

a perfect insulator instead of a perfect conductor. At first Kronig assumed that the rigid electron lattice could move as a whole through the metal, but, as he himself has shown,⁸⁵ this hypothesis soon proves untenable. The potential field in which the electron lattice moves is, apart from the temperature fluctuations considered above, the periodic field set up by the ionic lattice. This presents a potential barrier opposing the motion, which, if the total number of ions bound in the lattice is N , will be roughly N times as great as that opposing the motion of a single electron. Since the quantum-mechanical probability per unit time that a particle will pass a potential barrier decreases approximately exponentially with the height of the barrier, the probability that the electron lattice will be bodily displaced by an external field becomes vanishingly small even for quite small values of N . If, however, one considers a one-dimensional electron lattice, this does not necessarily follow. For the sake of simplicity the one-dimensional lattice is taken for the zeroth approximation as a closed ring in which $2N$ points (the electrons) which exert forces upon one another are equally spaced at intervals a . If the interactions only of adjacent points are considered, the problem proves capable of explicit solution and the eigenfunctions can be written down. The perturbation of this by the one-dimensional ionic lattice is now represented by means of a periodic potential

$$U = \sum_r A_r \cos \frac{2\pi_r X}{a},$$

with period equal to the separation between the electron points. The matrix elements for the first term in the Fourier expansion of the perturbation energy, summed over all the electrons, are of the form

$$K = \frac{A}{(\gamma N)^{a^2 b \sqrt{m}}}$$

for N large, where γ is a mathematical constant. Further consideration shows that the electron lattice can move readily only if K decreases with increase of N at least as rapidly as $1/N$. The

criterion for possibility of an actual superconduction current is therefore $2\hbar/a^2b\sqrt{m} \geq 2$ where b is the elastic constant which determines the vibrations of the electrons about their position of equilibrium and which appears as a parameter in the eigenfunctions. For the model under consideration, with purely electrostatic forces between the electron points, $b = \sqrt{2e^2/a^3}$ and finally the critical distance of separation becomes $a \leq \hbar^2/2e^2m$, which amounts to a few Ångstrom units.

One is finally led to the following conception of a superconducting metallic crystal. Below the transition point the conduction electrons form a rigid lattice within, and independent of, the ionic lattice. This as a whole is fixed in position, but single chains of electrons are free to move along their length, and under the influence of an external electric field more or less of them will do so. The idea in its final picture is, therefore, perhaps the quantum-mechanical analogue of the semi-classical model of Benedicks. The superconducting temperature is the "melting-point" of the electron lattice, determined by the thermal motions of the electrons alone. This temperature may be expected to be sharply defined just as is the melting-point of an atomic crystal.

Under an external magnetic field the electron lattice will be perturbed and will gain energy so that the thermal agitation necessary to melt it is reduced. With high frequency currents, also, the electron lattice will gain energy by absorption of quanta of the corresponding electromagnetic waves. Since the atomic lattice is not disturbed in the transition to the superconducting state, there should be no appreciable discontinuity in its non-electrical properties other than a possible small anomaly in the specific heat such as that recently observed for tin. In particular, there could be no sudden increase in thermal conductivity, due to the removal of resistance to the motions of the electrons, since below the transition point the electrons are incapable of exchanging energy with the ions.

A further support to the theory lies in its indication that the electron chains will be free to move only if the separation of the electrons in the chain is less than a certain distance which turns out to be of atomic dimensions. It would, therefore, be expected

that the elements which are most likely to show superconductivity are those of low atomic volume, and preferably those with several easily removable valence electrons. But these properties are also characteristic of the central columns of the periodic table, and are possessed by all known pure superconductors.

Dorfman's Hypothesis. Dorfman⁸⁶ in his treatment of the problem makes no attempt to devise a definite model of a superconducting metal, but seeks rather to derive the various experimentally observed phenomena from a single simplifying hypothesis of a mathematical nature. This assumption is that there are two distinct energy states possible for the conduction electrons, of which the lower W corresponds to superconductivity and the higher W' to ordinary conduction accompanied by electrical resistance. One thinks, perhaps, of a change of state affecting only the conduction electrons, the upper state being the Fermi electron-gas and the lower something analogous to a liquid or a solid.

This hypothesis can be taken as a consequence of several different metallic models, for example, of the conception, which Dorfman ascribes to Einstein, of coupled electron swarms. This coupling of the conduction electrons is supposed to take place spontaneously, somewhat in analogy with the spontaneous magnetisation of Weiss's theory of ferromagnetism. In fact, this apparent analogy between superconductivity and ferromagnetism has been pointed out by several authors, and attempts have been made to explain superconductivity on this basis. However, there are essential differences between the two phenomena and a too direct parallel is misleading. This conception of spontaneous coupling is, of course, just that which has been made very much more definite by Kronig, and the consequences to be drawn in the following from Dorfman's hypothesis can be applied directly to Kronig's model. The energy difference $W_i = W' - W$ is here the energy lost when a free electron becomes bound in the electron lattice or coupled swarm.

Another conception, at first sight entirely different, is ascribed by Dorfman to Schubin. It is here assumed that the scheme of energy levels for the conduction electrons of a superconductor consists of a series of broad permitted bands with forbidden inter-

vals between, as opposed to the continuous system of energy levels of the electron gas. At the lowest temperatures the lowest energy bands will be completely filled, and there will be no electrons in the higher bands. At slightly higher temperatures, the electrons will accumulate a certain amount of energy and will congregate towards the upper limits of the bands, but may not yet be able to acquire the energy W_i necessary to transfer them to a definitely higher band. According to Bloch's theory of ordinary conduction, an electron can only give up its energy to the ionic lattice when this energy contribution exceeds a certain minimum. If this minimum energy is greater than the breadth of the permitted band, the electrons cannot give up energy to the lattice until some at least of them have been excited to higher bands, and the model may, therefore, become superconducting for suitable relations between the energy values concerned. It is interesting in connection with this idea to note that the energy levels of the one-dimensional lattice treated by Kronig have just this form, of broad bands with forbidden intervals, in the case where the chain is capable of easy displacement along its length.

We shall now consider Dorfman's hypothesis without reference to any definite physical model. As a matter of convenience only the energy difference W_i between the two assumed states will be referred to as the coupling energy. At a temperature T the mean kinetic energy of the conduction electrons is $U = U_0 + U_T$ where U_0 is the zero-point energy. With increase of temperature this increases, but as long as $U_T < W_i$ it may be maintained that the electrons will remain in the lower state. When U_T increases beyond W_i the upper, ordinarily conducting, state is so to say excited. The superconducting transition point θ is, therefore, given by $U_\theta = W_i$. For statistical reasons there still remains some difficulty in explaining, according to this simplified conception, the sharpness of the transition. Dorfman suggests that this sharpness is only apparent, that actually the true critical temperature is somewhat higher than that observed but that superconductivity is not realized for a sample of finite size until a sufficient number of atoms have passed into the lower superconducting energy state to form a continuous thread throughout the material. The tem-

perature where a certain fairly large fraction are in the lower state will, of course, be sharply defined. There may be some support for this view in the fact that in most cases a small quantity of an impurity lowers the superconducting point and makes the transition less abrupt.

If a superconductor is subjected to a magnetic field H , each conduction electron acquires an additional energy $W_H = \pm \mu H$ where μ is the spin moment of the electron. At a temperature $T < \theta$ the additional energy necessary to excite the uncoupled state will be $W_i - U_T$ so that the magnetic field necessary to restore the resistance is given by

$$H_T = \frac{1}{\mu} (W_i - U_T).$$

According to theory of metals, for sufficiently low temperatures, $U_T = cT^2$ and we have $W_i = U_\theta = c\theta^2$, so that

$$H_T = \frac{c}{\mu} (\theta^2 - T^2)$$

in agreement with the empirical law found by Onnes and others.* It is not unreasonable to assume that the effect of high frequency currents is essentially due to absorption of the corresponding electromagnetic wave. If the quantum $h\nu$ of the wave is not sufficient to excite an electron into the upper energy state, the metal will act as a perfect reflector, but if $h\nu \geq W_i - U_T$, energy will be absorbed and the resistance will be restored. Again the theoretical law takes the form

$$\nu_T = \frac{c}{h} (\theta^2 - T^2)$$

where ν_T is the critical frequency which annuls the superconductivity at a temperature T . Dorfman⁸⁶ has shown that the

*Some results on the effect of a magnetic field appear to agree better with a linear law of the form

$$H_T = a(\theta - T).$$

The form of the theoretical law naturally depends upon the function assumed for U_T .

earlier results of McLennan and others⁵⁰ agree very well with a law of this form.*

The constant c involved in the above formulae can be calculated from the empirical data for the superconductivity of tin, either from the experiments upon the magnetic field effect, or from those of McLennan on high frequency currents. We have, on the one hand, $c/\mu=20.3$, and on the other hand $c/h=2.87.10^7$, giving $c=1.874.10^{-19}$ and $1.882.10^{-19}$ respectively. As Dorfman remarks, this surprisingly close agreement is probably partly accidental, especially in view of the more recent experiments with high frequency currents. The constant is also given according to Sommerfeld's theory by the formula

$$c = \frac{\pi^2 m k^2}{h^2} \left(\frac{8\pi}{3N} \right)^{2/3} \left(\frac{V}{n} \right)^{2/3}$$

where V is the atomic volume, N is Avogadro's number, and n is the number of conduction electrons per atom. From this and the empirical results for the effect of a magnetic field on superconductivity, it is possible to estimate the fraction of the electrons which take part in the phenomenon, with the following results:

Metal	c/μ	
Lead	24	0.018
Tin	20.3	0.021
Mercury	25.16	0.015
Thallium	25.4	0.017

This appears to indicate that superconductivity is realized when from 1.5 to 2 per cent. of the valence electrons are in the lower energy state.

The existence of a coupling energy of the kind here proposed will cause an anomaly in the specific heat of the metal in the neighbourhood of the transition temperature θ . An estimate shows, however, that in view of the small number of electrons which are

*By analogy Dorfman suggests that ferromagnetism should be annulled by waves of sufficiently high frequency. For iron at 300°K the critical frequency would correspond to a wave-length of about 12μ , and the phenomenon might be made manifest by an anomalous behaviour of iron towards infra-red radiations of longer wave-length.

apparently involved this would amount to only about one per cent. of the total specific heat. Moreover, it might occur at a temperature slightly above the superconducting point where it has hitherto been sought. Such an anomaly has been observed for tin, but the most careful measurements of Simon and Mendelssohn⁸⁶ have failed to reveal it for lead. It is well known, however, that the specific heat anomaly at the Curie point for a ferromagnetic substance is always accompanied by a change in the thermoelectric properties, especially in the Thomson coefficient. Borelius and others⁸⁷ have actually observed a marked maximum in the Thomson coefficient for lead at a temperature of 10.5°K , possibly supporting also Dorfman's idea that the true transition temperature is higher than the superconducting point.

The idea that the sharpness of the transition is only apparent and that the electrons in reality pass gradually into their lower energy state, as would be expected on statistical grounds, may have some bearing on the experiments of de Haas and Bremmer⁸⁸ on the thermal conductivity. If the electrons in the superconducting state are incapable of exchanging energy with the ions, one would expect a marked *decrease* in the thermal conductivity at the electrical superconducting point. The experiments show that the change of thermal conductivity at the actual transition temperature is small and may take place in either direction for different metals. At still lower temperatures, however, the thermal conductivity decreases continuously and rapidly becomes very small.

Landau's Treatment. There is undoubtedly still a considerable difficulty in reconciling any model of a superconducting metal with thermodynamical considerations and with the recent successful theories of ordinary conduction. For the latter the general point of view taken in the papers of Kronig and Dorfman is probably the most promising that has so far been suggested. It cannot yet be said with certainty, however, that the considerations would remain valid under a more detailed examination from a thermodynamical point of view.

Landau⁸⁹ in particular has emphasized this point, and has attempted an alternative method of treatment derived directly from thermodynamical considerations. The fundamental assump-

tion made is that, below the superconducting temperature, the thermodynamically most probable state of the metal is not the ordinary state with zero current, but a state in which the local current density attains a saturation value. This, of course, does not necessarily lead to a macroscopic current in the absence of an external electric field. The free energy F can be expressed as a function of the temperature and of the local current density in the form

$$F(T, i) = F_0(T) + \frac{1}{2}m(T)i^2 + \frac{1}{4}n(T)i^4 \dots$$

for it can be shown on grounds of symmetry that odd powers of i cannot appear in the expansion. If $m(T) = \beta^2(T - \theta)$ and n is positive in the neighbourhood of θ then F will be a minimum for $i=0$ when $T > \theta$ and for $i=i_{sat.}$ when $T < \theta$. A distribution of local currents which will give saturation density without macroscopic flow can be determined by consideration of classical electrodynamics, and the effect on this of an external magnetic field can be shown to lead to the correct behaviour.

Landau has not suggested any metallic model for which the free energy would be of the form supposed, and this might, indeed, be difficult to reconcile with known facts of metallic structure. However, it is evident that we can find in this conception also the two energy states of Dorfman's hypothesis, the state of free electrons, and the state where the electrons are coupled in the lines of saturation current. Possibly, therefore, Landau's treatment is not incompatible with other recent treatments, and it may, indeed, point the way to a thermodynamical justification. Much still remains to be done before an entirely satisfactory solution of the difficult problem is attained, but it can at least be said that very considerable progress has at last been made.

APPENDIX

VALUES OF RESISTANCE RATIOS FOR THE ELEMENTS

Metal	T °K	$\frac{R}{R_0}$	Metal	T °K	$\frac{R}{R_0}$
Li	1.19	0.0058 ⁵	Th	4.22	00.170
Na	1.23	0.00375	Ge	1.22	1.289
K	1.22	0.00693	Sn	4.20	0.00079
Rb	1.13	0.0346	Pb	7.3	0.0010
Cs	1.15	0.0395	V	1.25	0.429
Cu	1.32	0.00029	Ta	4.5	0.0099
Ag	2.0	0.00288	As	1.13	0.0211
Au	1.34	0.00029 ¹	Sb	1.16	0.01805
Be	1.35	0.3077	Bi I	1.05	0.0042
Mg	1.27	0.0329	Bi II	1.33	0.0027
Ca	1.36	0.2792	Cr	2.25	0.0526
Sr	1.32	0.0932	Mo	1.51	0.0462
Ba	1.26	0.0446	Wo	1.31	0.00053
Zn I	1.67	0.00174 ⁶	U	1.41	0.5400
Zn II	1.67	0.00181 ³	Te	1.13	0.5470
Ca I	1.35	0.00047 ⁵	Mn	1.41	0.958
Ca II	1.35	0.00015 ⁷	Rh	1.36	0.109
Hg	4.33	0.00206	Fe	1.98	0.00618
Al	1.31	0.0067	Ru	1.17	0.0827
In	4.21	0.00387	Co	1.51	0.0431
Tl	4.22	0.000537	Rh	1.31	0.00300
C(graphite)	1.15	0.1193	Ir	1.29	0.0478
Ti	2.01	0.1047	Ni	1.34	0.00503
Zr	1.35	0.0384	Pd	1.17	0.00559
Hf	1.35	0.0947	Pt	1.35	0.00165
Ce	1.43	0.697			

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